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L. I. Belenky •

While the spectrophotometric method of analysis of water-soluble dyes has already been used for scientific and technical purposes for many years [1], its application to insoluble dyes and pigments meets a number of difficulties. The main difficulty was in bringing such dyes into solution and in the instability of technically utilized leuco solutions. The literature contains only a few publications and discussions of spectrophotograms of solutions of polycycloketonic dyes [2] and indigo [3].

We proposed the use of sols of insoluble dyes [4], including dyes of the classes in question, for spectrophotometric and colorimetric investigation. The electron spectra of solutions of complex organic compounds, such as vat and sulfur dyes, are fairly complicated, and conversion into sols is associated with further changes of optical properties. Nevertheless, optical study of sols is appropriate on the basis of the following experimental data and methodological considerations:

1. In a considerable number of cases the absorption spectra of colloidal solutions are more selective and have more clearly defined maximum and minimum values than the corresponding spectra for molecular solutions.
2. The synthesis of dye sols, if suitable conditions are observed, gives well reproducible stable dispersions with constant (within definite limits) optical properties. The absorption spectra of the sols show good reproducibility.
3. The stabilization of sols by protective substances creates conditions which favor a linear relationship between the concentration and the light absorption of sols (Beer's law [5]).

The present paper contains the results of spectrophotometric investigation of colloidal solutions of a series of vat and sulfur dyes.

The investigations were carried out with samples of specially prepared, purified dyes and with the usual technical dyes. Polycycloketonic vat dyes were purified by recrystallization from organic solvents (for example, ortho-dichlorobenzene), and in some cases by consecutive extraction of the technical products with alkalis, water and ethanol. Sulfur dyes, which are essentially complex mixtures of amorphous high molecular substances, were purified by repeated separation from the leuco solutions ("revatting")**. The purified products, in agreement with literature data, were checked by their X-ray diagrams [6] and chromatograms [7] in aluminum oxide columns.

The colloidal sols were prepared mainly by condensation from leuco solutions, solutions in sulfuric acid, etc. In some cases dispersions of special powders (stable suspensions) were used.

The spectrograms were mostly obtained with the aid of a photoelectric spectrophotometer of the Beckmann type. Some of the measurements were made with a Hardy recording spectrophotometer, and the König-Martens polarizing apparatus. In some cases colorimetric measurements were made with a differential photocolormeter with selenium photocells. The individual auxiliary methods and apparatus are described below in the descriptions of the corresponding experiments.

The ordinates of the spectrophotograms show the values of the extinction coefficient $E = \log \frac{I_0}{I}$, as the values of molal extinction could not be calculated for all the dyes.

EXPERIMENTAL

a) Vat dyes. The object of the experiments was to elucidate the specific peculiarities of the absorption spectra of colloidal dispersions, to compare them with absorption spectra of molecular solutions, and to investigate the applicability of Beer's law and the possibility of using the spectrophotometric method for chemical analysis. The experiments were carried out with a large number of dyes from different groups (indigoid, aminoanthra-

* The experimental work was carried out by M. E. Kazanskaya

** We are indebted to A. A. Myasnikov for the preparation of purified specimens of sulfur dyes.

quinone, indanthrone, benzanthrone, dibenzopyrenequinone, and violanthrone derivatives, etc.). The reproducibility of the spectrophotometric curves was verified by repeated experiments. The observed errors are not caused so much in the preparation of the sols as by the extent of solution in the first stage (solution in sulfuric acid or leuco

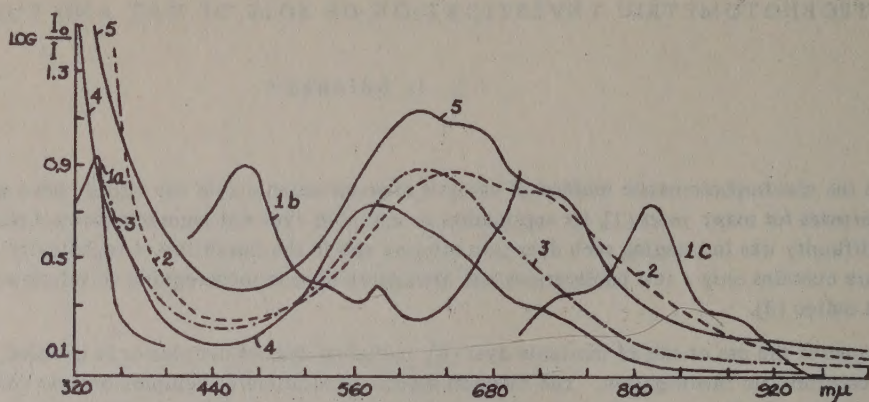


Figure 1. Spectrophotograms of Vat Sky Blue K: 1) Solution in sulfuric acid, ϕ .gr 184 (1a - 20; 1b - 100; 1c - 200 mg/l); 2) leuco solutions, 100 mg/l; 3) hydrosol, 100 mg/l; 4) hydrosulfo sol, 100 mg/l; 5) aqueous suspension, 200 mg/l.

solution) and by the extent to which the prescribed conditions are maintained. In one of the most complex cases (hydrosols from leuco solutions of Vat Bright Green), in four-fold repetition of the sol synthesis, the error (from the area under the spectrophotometric curve) was $\pm 1.5\%$. In the case of hydrosulfo sols the error decreases to $\pm 1\%$.

Figure 1 shows spectrophotograms of colloidal and molecular solutions of Vat Sky Blue K. The experiment shows that while the separate spectrophotograms show good reproducibility, they differ considerably from each other, which indicates differences in the absorbing particles. The considerable differences of the absorption spectra of solutions in sulfuric acid may act as confirmation of the presence of sulfonoxides, discovered by Lukin [2]; the appearance of a well-defined absorption band in the near infra-red (820 mμ) is characteristic. A greater similarity is shown by absorption spectra of the leuco solution, hydrosol, hydrosulfo sol, and the aqueous suspension of the dye obtained by dilution with water of a specially prepared finely dispersed powder. The absorption spectrum of the aqueous solution is unchanged on further dilution with water; the absorption spectra of the hydrosols and hydrosulfo sols are also unchanged on dilution.

The absorption spectra of sols sensitively reflect structural peculiarities of the dyes, as has long been known for molecular solutions.

A spectrophotometric characterization of structural differences is shown in Figure 2, on the example of absorption curves of brominated indigo hydrosulfo sols.

The introduction of bromine in the indigo molecule significantly affects the dyeing properties; the absorption spectra of the brominated products are also changed. The details of these products (as a rule, technical grades, but containing up to 90% pure dye), the sole concentrations, and the composition of the protective colloid are given in the caption to Figure 2. The following conclusions may be drawn from an examination of the spectrograms.

1. The light absorption of the sols clearly reflects even small differences of molecular structure.
2. Increased complexity of the molecule (increase of the degree of bromination) produces a hypsochromic effect — a shift of the maxima of the absorption bands into the short wave region; the only exception was the sol of monobromindigo protected by OP-10, which proved insufficiently stable.
3. The absorption spectra of the sols are largely determined by the nature of the protective agent, that is, by the structure of the colloidal particle (see, for example, curves 2 and 3 in Figure 2).
4. The absorption spectra of hydrosulfo sols change during the first few hours after preparation and become

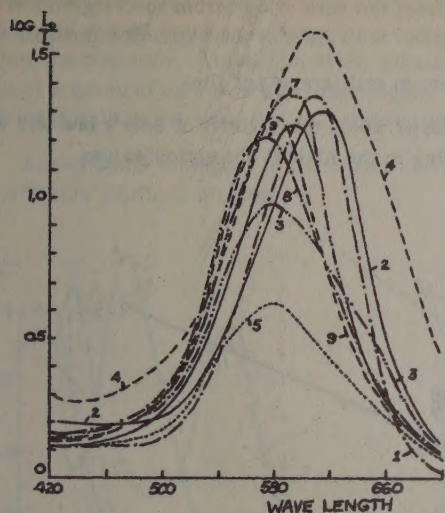


Figure 2. Absorption spectra of brominated indigo preparations (hydrosulfo sols): 1) Indigo, 20 mg/l, Emulphor as protective colloid; 2) monobromindigo, 60 mg/l, OP-10; 3) ditto, 100 mg/l, Emulphor; 4) dibromindigo, 60 mg/l, Emulphor; 5) indigo KG (mixture of hexa- and pentabromindigo), 30 mg/l, OP-10; 6) dichlorodibromindigo, 60 mg/l, OP-10; 7) CIBA Sky Blue 3B, 60 mg/l, Emulphor; 8) tetrabromindigo, sample A, 80 mg/l, OP-10; 9) ditto, Sample B, 80 mg/l, OP-10.

Sols of the dyes considered in the present paper have no clearly defined turbidity or opalescence; they are transparent. The turbidity determined by Tyndallometric measurements is very small. Nevertheless, the presence of light scattering, in consequence of the polarization of scattered light, may be shown by comparison of spectrograms obtained with the polarization spectrophotometer and with the photoelectric spectrophotometer, which has no polarizing system. The results of such a comparison (for the same solutions) are shown in Figure 3, where a and b are spectrograms obtained with the photoelectric apparatus and with the usual visual polarization spectrophotometer. The difference between the spectrograms is clear not only in the case of tetrabromindigo hydrosulfo sol (curve 1) but also for the usual aqueous solutions of direct dyes (curves 2 and 3), and the nature of the differences is the same in these experiments; we must point out that this effect does not prevent spectrophotometric analysis of water-soluble direct dyes.

stabilized after 6-10 hours. This last conclusion is based on extensive experimental data, which was not included (for the sake of limitation of space) in the curves shown. Apparently gradual hydrolysis of sulphonoxides and formation of colloidal particles takes place.

In production conditions (in the synthesis of dyes) it is probable that a certain mixture of bromine derivatives is obtained. It should be noted that the spectrophotometric curves of the hydrosulfo sols of brominated derivatives show good reproducibility; the maximum deviation between parallel determinations (areas under the curves) does not exceed 1-2%.

The use of dye sols for spectrophotometry raises the question of the validity of the use of such sols for light scattering investigations. It is well known that colloidal systems not only absorb light, but scatter it in agreement with the Rayleigh equation (Tyndall effect) [8]. There have also been attempts to modify the Beer's law equation [9] for colloidal systems

$$I = I_0 e^{-\frac{kVcd}{\lambda^4}},$$

where I and I_0 are the intensities of the scattered and incident light respectively, k is the absorption constant; V is the particle volume; cd is dye concentration, λ is the wave length of the scattered light.

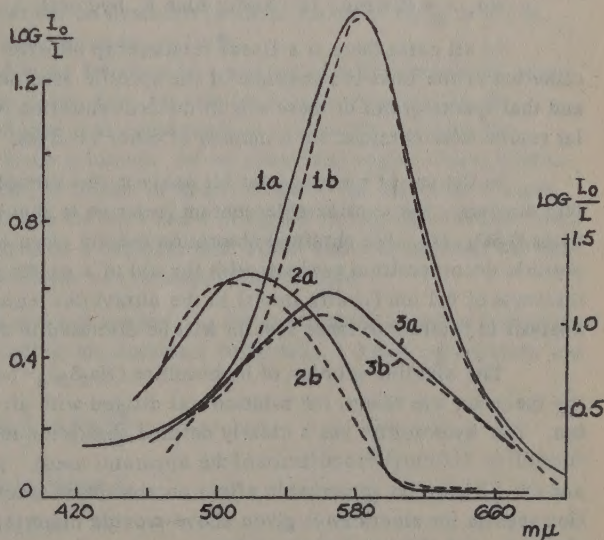


Fig. 3. Comparison of absorption spectra obtained with the photoelectric (a) and polarization (b) spectrophotometers: 1) Hydro-sulfo sol of tetrabromindigo, 80 g/l; 2) solution of Direct Rose 2C; 3) solution of Direct Blue M.

Figure 4 shows the results of a verification of Beer's law from the data of numerous spectrograms of vat dyes, obtained for sols of different concentrations. The ordinate axis shows the values of the extinction coefficient $E = \log \frac{I_0}{I}$, and the abscissa axis shows the solution concentrations in milligrams per liter.

The caption to Figure 4 gives a list of the dyes for the sols of which the validity of Beer's law was verified, and shows the wave lengths for maximum absorption, corresponding to the highest absorption values.

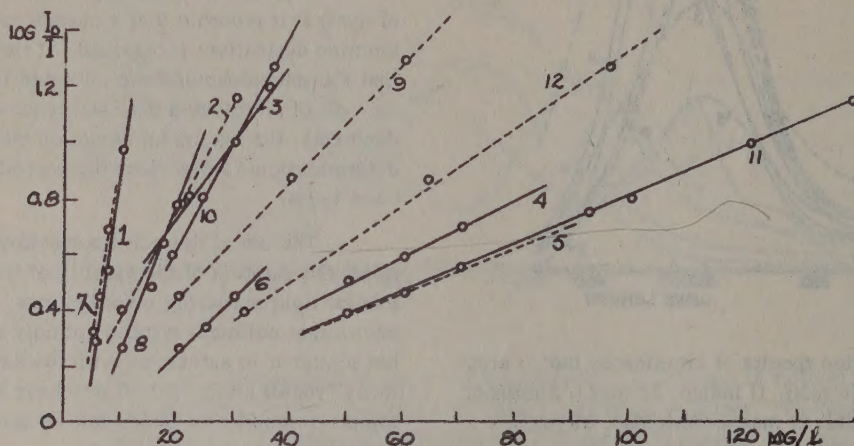


Figure 4. Beer's law for sols of vat and sulfur dyes: 1 and 2) Hydrosols of indigo (with different protecting agents $\lambda = 663 \text{ m}\mu$; 3) Vat Bright Green S, hydrosol, $\lambda = 620 \text{ m}\mu$; 4) Vat Blue VS, $\lambda = 590 \text{ m}\mu$; 5) ditto, hydrosulfo sol, $\lambda = 590 \text{ m}\mu$; 6) ditto, imported sample, $\lambda = 590 \text{ m}\mu$; 7) Vat Bright Green S, hydrosulfo sol, $\lambda = 617 \text{ m}\mu$; 8) Vat Bright Violet K, hydrosol, $\lambda = 540 \text{ m}\mu$; 9) ditto, purified, hydrosol, $\lambda = 525 \text{ m}\mu$; 10) ditto, Green FFB, hydrosol, $\lambda = 620 \text{ m}\mu$; 11) Sulfur Black, hydrosol, $\lambda = 620 \text{ m}\mu$; 12) Sulfur Blue K, hydrosol, $\lambda = 570 \text{ m}\mu$.

In all cases there is a linear relationship between the absorption and the concentrations; the angle of inclination of the lines is a measure of the specific absorption. It follows that Beer's law holds for sols of vat dyes and that spectrograms of these sols in the concentration region studied may be used for analytical purposes. Similar results were obtained for a number of other vat dyes.

In the use of spectrograms for analysis, the complex electrolyte composition of the media must be taken into account: the considerable content (relative to that of the dye) of $\text{Na}_2\text{S}_2\text{O}_4$, Na_2SO_3 , NaOH , OP-10, in some cases H_2SO_4 , etc. We obtained absorption spectra of an alkaline solution of chemically pure hydrosulfite and its possible decomposition products with the aid of a quartz photoelectric spectrophotometer, with a solution layer thickness of 0.1 cm (quartz insert) in the ultraviolet region of the spectrum (Figure 5). Questions of structure analysis in relation to these spectra will be discussed in another paper.

The alkaline solution of hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$ —50 g/l, NaOH —46 g/l) was stored 3.5 hours in a closed flask before the spectrum was taken; the solution was diluted with air-free water in the ratio of 1:100 before the determination. The hydrosulfite has a clearly defined absorption maximum at $\lambda = 320 \text{ m}\mu$; sodium sulfate at $230 \text{ m}\mu$, sulfite and thiosulfite, $210 \text{ m}\mu$ (beyond limits of the apparatus used); potassium metabisulfate, $\lambda \approx 260 \text{ m}\mu$; NaOH , H_2SO_4 , and OP-10 have no appreciable effect on absorption spectra in the conditions of our experiments. The absorption spectra for electrolytes given above provide material for the interpretation of absorption spectra of sols, solutions, and leuco-solutions of dyes.

The spectrophotometric method provides possibilities for the study of reduction and neutralization processes and other physico-chemical changes in the molecules of vat dyes. As an example, Figure 6 shows the conversion of the leuco compound of Indanthrene Bright Green FFB into the "vat acid" on neutralization with acetic acid in presence of a protective agent — purified sulfite liquor. The neutralization process was controlled with a glass electrode and an electronic pH meter. Because of the instability of the neutralized solutions the

spectrophotometric measurements were made with a recording spectrophotometer (each curve was recorded in 2.5 minutes) and the pH value was determined twice — before and after the spectrogram was obtained. It is possible to follow the transition of one form of the alkaline leuco compound (curve 1) into another (curve 8) by the intersection of a group of curves in a definite region. Similar equilibrium phenomena between two forms were discussed previously in the literature for water-soluble dyes [10].

Experiments analogous to those shown in Figure 6 were also carried out with other dyes: Vat Blue VS, Vat Golden Yellow ZhKh, and indigo.

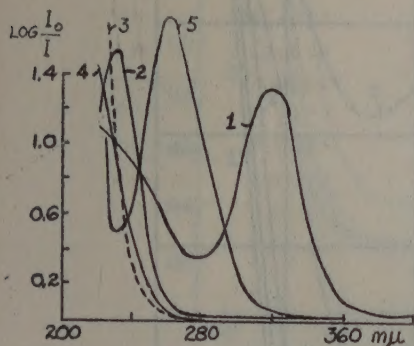


Figure 5. Absorption spectra of a solution of hydrosulfite and its possible decomposition products. 1) Alkaline solution of hydrosulfite, 0.5 g/liter; 2) sodium sulfate, 0.2 g/liter; 3) sulfite, 5 g/liter; 4) hyposulfite, 1 g/liter; 5) potassium metabisulfite, 10 g/liter (taken in cuvette of 10 mm diameter).

Sulfur dyes. The problems which arise in spectrophotometric investigation of sulfur dyes are analogous to those formulated for vat dyes. They are made complicated, on the one hand, by the indefinite molecular structure of the dyes in this class, and on the other, by the lack of stability of the processes of leuco compound formation. Each conversion into a leuco solution is accompanied by the loss of a certain amount of structural sulfur. However, it is because of the instability of sulfur dyes that spectrophotometric methods, which do not involve any chemical action on the solutions, should be the most practicable.

The reproducibility of the spectrophotometric curves for different sulfur dyes is not the same. The hydrosols of certain of the dyes, mainly black, which contain excess H_2O_2 , undergo slow oxidation of organically combined sulfur and, at the same time, a change in the absorption spectrum; the extent of the change depends on the excess of H_2O_2 . If Na_2SO_3 is added to the hydrosols to take up the excess H_2O_2 , it is possible to obtain practically constant (within the limits of 24 hours) absorption spectra from dinitrochlorbenzene even in the case of the oxidation-sensitive Sulfur Black.

The mean relative error in parallel spectrophotometric determinations on hydrosols (without excess of H_2O_2) is $\pm 1\%$, and for leuco solutions, $\pm 1.5\%$.

Figure 7 shows absorption spectra of hydrosols and leuco solutions of a number of sulfur dyes in the ultraviolet and visible regions of the spectrum. As in the case of vat dyes, the spectra clearly characterize the structure of these substances (that is, a definite absorption spectrum corresponds to each sulfur dye) and the specific absorption of the sols is greater than that of the leuco solutions. In the ultraviolet region characteristic absorption bands are due to the presence (in leuco solutions) of sulfide or hydrosulfide; if the reduction is more extensive (with hydrosulfite), the absorption is intensified (see curves 2 and 4 of Figure 7). Aging of sulfide leuco solutions (like the aging of sulfide solutions) is accompanied by a hypsochromic effect and a diffusion of the short wave absorption band; these effects are apparently characteristic of the polysulfides formed.

Beer's law was verified for all the leuco solutions and sols studied. In the concentration region investigated, which was determined by the solubility and spectrophotometric measurement conditions, a linear relationship was found between the values of the extinction coefficients

$$\kappa = \log \frac{I_0}{I} = \log \frac{I_0}{I}$$

and the concentration. The experimental data are shown in Figure 4.

DISCUSSION

The results presented in this paper confirm the views put forward in the introduction. Despite the complexity of the relationship between the degree of dispersion, solvation, stability and the extinction coefficients of sols of vat and sulfur dyes, these sols are analytically reproducible in appropriate conditions. For colloidal solutions Beer's law is confirmed by a proportionality between the extinction coefficients and the corresponding concentrations.

The absorption spectra of sols of vat and sulfur dyes are as definite physical characteristics of their

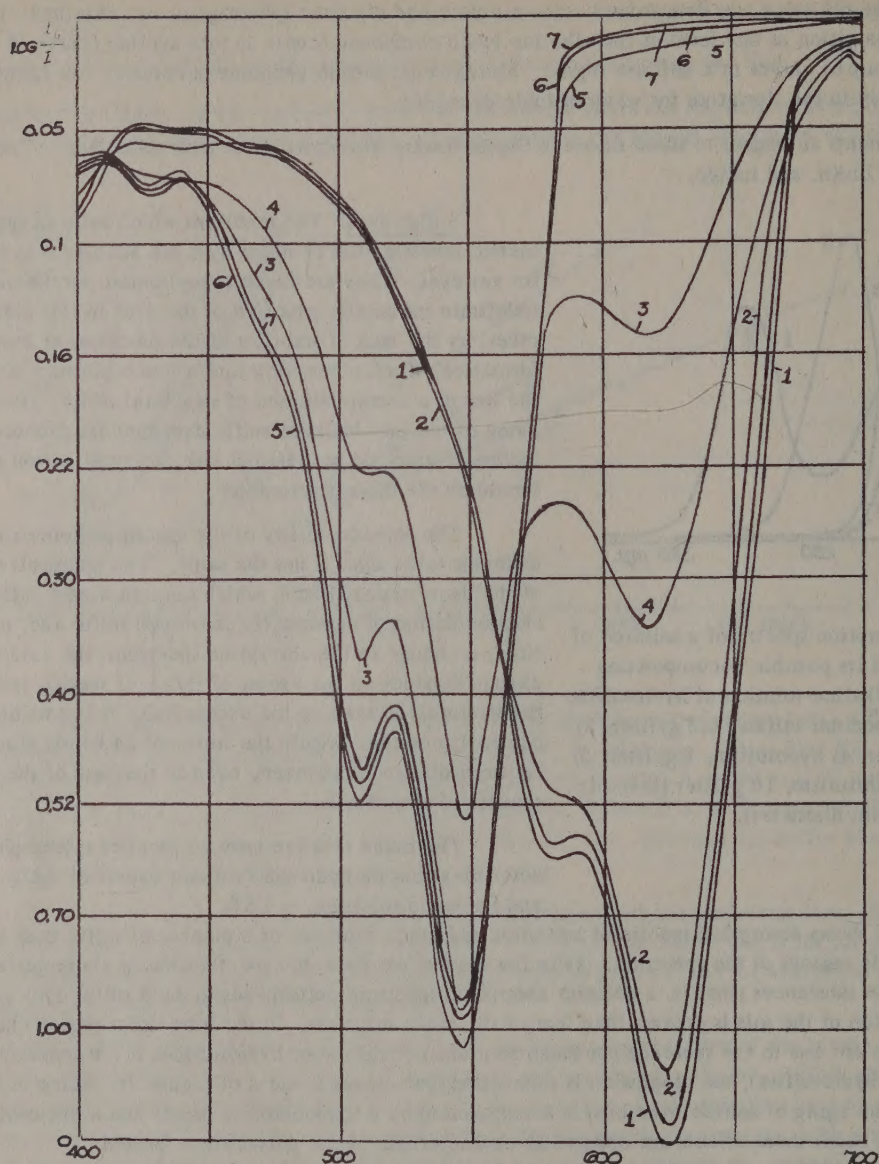


Figure 6. Absorption spectra of leuco solutions of Indanthrene Bright Green FFB during neutralization by acetic acid at pH values: 1) 11.8; 2) from 11 to 10.9; 3) from 8 to 7.85; 4) 9.5; 5) from 7 to 6.75; 6) from 5.5 to 5.45; 7) 4.5.

structure as is the case for spectra of soluble dyes. The relationship between the spectrophotometric and the dyeing properties of the dyes was not considered in this study. This relationship is made complicated in the case of sulfur dyes because of the instability of their composition, and it arouses no doubts in the case of vat dyes. The absorption bands of sols and leuco solutions in the ultraviolet region are largely determined by reducing agents: $\text{Na}_2\text{S}_2\text{O}_4$ and Na_2S . The extinction coefficients of these substances (as was established by special experiments) are also proportional to the concentration, which raises the possibility of their spectrophotometric determination. The observed hypsochromic shift and widening of the absorption band ($\sim 230 \text{ m}\mu$) for oxidized (aged) solutions of Na_2S and leuco solutions of sulfur dyes is apparently associated with the formation of polysulfide chains.

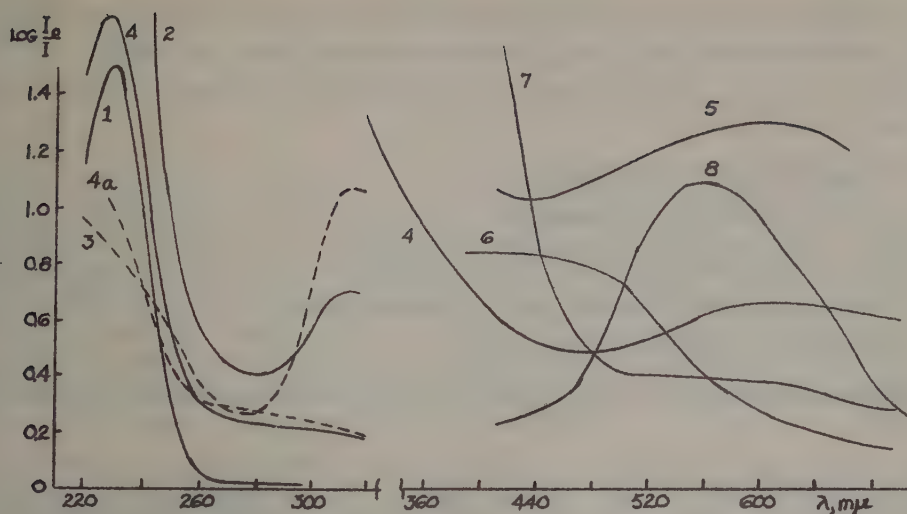


Figure 7. Absorption spectra of leuco solutions and hydrosols of sulfur dyes: 1) Sodium sulfide, 160 mg/l, $d = 1$ mm; 2) Sulfur Black (purified) leuco solution, 100 mg/l, diluted with alkaline hydrosulfite, $d = 1$ mm; 3) control solution K-2, NaOH 0.5 g/l, $\text{Na}_2\text{S}_2\text{O}_4$ 0.4 g/l; 4) Sulfur Black, purified, leuco solution, 100 mg/l (without $\text{Na}_2\text{S}_2\text{O}_4$), $\lambda = 220-320$ mμ, $d = 1$ mm; $\lambda = 320-700$ mμ, $d = 10$ mm; 4a) the same, 6 hours after preparation; 5) Sulfur Black - purified hydrosol, 100 mg/l; 6) Immedial Dark Brown A, hydrosol, 100 mg/l; 7) Sulfur Blue 3, leuco solution, 800 mg/l; 8) the same, hydrosol 100 mg/l.

The group of experiments on the investigation of the neutralization of leuco solutions (Figure 6) could be carried out by virtue of automatic recording of the spectra, as the solutions formed are unstable. It should be noted that a sharp hypsochromic shift of the absorption spectra is observed in the transition from sodium leuco compounds to leuco acids in all cases. This shift is in agreement with earlier observations on polymerizing water-soluble dyes (for example, polymethines [10]) and indicates behavior which is apparently associated with a volume increase of the dissolved particles (decrease of the degree of dispersion).

The results obtained are evidence of the possibility of spectrophotometric and colorimetric analysis of vat and sulfur dyes in the determination of the dynamics of concentration variations during dyeing, and for the evaluation of the concentration and qualitative identity of commercial products. The preparation of pure dye samples for the determination of their specific extinction coefficients is important.

SUMMARY

1. Methods were developed for the preparation of stable and reproducible sols of vat and sulfur dyes.
2. Absorption spectra of sols of a number of pure and technical vat and sulfur dyes in the range 220-700 mμ, and also the absorption spectra of the accompanying electrolytes, were obtained
3. It is shown that the absorption spectra of these sols in concentrations used in practice follow the Beer-Bouguer law.
4. It is shown that the absorption spectra of colloidal sols clearly characterize differences in the molecular structure of the corresponding dyes.
5. The existence of a hypsochromic displacement of the absorption spectra during neutralization of alkaline leuco compounds of vat dyes was shown.

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ELECTROPHORETIC INVESTIGATION OF MECHANICAL IMPURITIES IN ENGINE OILS

S. V. Ventsel and S. G. Teletov

As was shown earlier [1], the mechanical impurities formed in engine oils during the action of the internal combustion engine are grouped in complexes containing organic and inorganic components. It was shown that removal of the impurities by filtration largely restores the original chemical structure of fresh oil. On this basis conclusions were drawn concerning the basic role of adsorption forces in the formation of impurity complexes in oil. Further treatment of the data (Table 1) in the same paper [1] showed that the restoration of the acid number of used oils as the result of filtration regularly depends on the concentration of carbenes and carboids, the acid number increasing with increasing content of these substances. This behavior confirms the adsorption of oxidation products of the oil on highly dispersed carbonaceous particles. However, a more detailed study of the structure of these complexes, their nuclei and envelopes, is of interest for practical purposes.

As is known, adsorption and orientation of organic molecules containing polar groups may confer a charge to the adsorbing surface. Thus, demonstration of the existence of a charge by electrophoretic investigation of the impurities would serve as a final piece of experimental evidence in favor of the view concerning the adsorption of the oxidation products. However, as the oil medium does not conduct electricity, the electrophoresis method could not be applied directly to used oil. We therefore attempted to apply electrophoretic investigations to aqueous suspensions of the mechanical impurities, previously degreased, obtained from used oils. In this indirect method we made the conditional assumption that the mechanical suspensions show similar behavior in oil and water media. A number of causes (desorption during degreasing, low stability of the aqueous suspensions, etc.) might result in a failure to confirm the existence of a charge in aqueous suspensions.

The mechanical impurities obtained from used oil (see Table) by filtration through an analytical filter of medium porosity were repeatedly treated with a degreasing solvent (nonethyalted aviation gasoline B-70, 0.8 liter per 0.5 g of the dried impurities). After degreasing, the mechanical impurities became of a granular carbonaceous appearance and had a dry (non-greasy) feel.

During the preparation of aqueous suspensions (concentration 1:50), in addition to a stable fraction, part of the impurity settled out and part passed into the upper layer. With increased time of wetting, some of the impurities which at first settled out passed into the suspension. The suspended fraction, which was a greyish-black, flocculent suspension, remained stable for a considerable time.

The charge was determined electrophoretically. When the sample was placed in the electrophoresis apparatus, a fairly clear separation boundary was obtained between the suspension and the auxiliary liquid (distilled water). In all the 10-12 experiments the charge on the suspension was negative.

Properties of Used Engine Oils

Engine from which the oil was taken	Type of oil	Working time of oil, hours	Mechanical impurities, %	Ash %	Acidity, in ml KOH per g
Tractor DT-54	Diesel oil	40	0.30	0.03	0.24
Tractor STZ-NATI	Autol 10	60	0.42	0.11	0.36
Automobile GAZ-51	Autol 10	35	0.15	0.06	0.21

As soon as a potential difference was applied (the voltage was 80 V, current strength in the cell, about 30 mA), there was a distinct displacement of the separation boundary between the

suspension and the auxiliary liquid (at the negative electrode) toward the positive electrode. There was also a tendency to displacement of the second separation boundary at the positive pole, but after a greater time interval due to the coarser state of dispersion of the particles in the suspension (and hence, a low "lifting" force). Some thickening of the suspension was observed in the bend of the U-shaped tube of the apparatus at the positive pole. A parallel experiment with the same suspension, but without application of a potential difference, showed that the suspension had fairly good kinetic stability; the level of both separation boundaries did not change in the course of several hours.

After 30-40 minutes, as the result of discharge, a sharp change of stability of the suspension takes place near the positive electrode, which leads to destruction of the separation boundary between the suspension and the auxiliary liquid and to a considerable fall in its level. Almost at the same time, formation and condensation of slightly brownish flocculent deposits in the lower part of the bend of the negative electrode was observed. From the behavior and appearance of these deposits they may be considered to be ferric hydroxide. Samples from both bends of the apparatus showed different contents of iron [reaction with $K_4Fe(CN)_6$].

From these experiments, the following structure may be postulated for the highly disperse particles of mechanical impurities in used lubricating oils from internal combustion engines. The basic constituent of the impurities is apparently polydisperse iron, to a considerable extent in the form of hydroxide. The particles of ferric hydroxide are stabilized in the oil phase, being coated with an envelope of carbonaceous particles. Such stabilized particles with a highly developed surface, distributed in the oil phase, form an effectively adsorbing component of the system. When the particles of the suspension adsorb molecules of organic acids, the nonpolar portions of the latter will be directed toward the oil phase. The formation of polylayers is also possible, which does not subsequently hinder the molecular sorption of asphaltenes and resins. All this increases the size of the particle and confers a loose structure to its outer layer.

As regards the stabilization of aqueous suspensions of these impurities, it is evident that in the aqueous phase, as a polar medium, "inversion of the adsorbed molecules" takes place, with the polar groups directed toward the more strongly polar phase [2], which stabilizes these suspensions in the aqueous medium and makes it possible to show the presence of a charge in electrophoresis.

Thus, the experiments carried out confirm the presence of a colloidal protective layer in the surface of the products of wear and other solid particles in used engine oils, which fully explains the previously discovered relationship between wear of engines and composition of the impurities [3].

SUMMARY

1. Stable aqueous suspensions of degreased mechanical impurities from used engine oils were obtained; the particles of the impurities had a negative charge in electrophoresis.
2. The complex nature and structure of the aggregated complex of the mechanical impurities was shown.
3. Views are put forward concerning the structure of the aggregated complex of the mechanical impurities in used engine lubricating oil, and their role as the adsorbing component in the restoration of oil properties by filtration is confirmed.
4. The presence of colloidal protection on the surface of the products of wear and other abrasive particles is confirmed.

Student assistant S. M. Kel participated in the experimental work.

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THE BEHAVIOR OF SUSPENSIONS OF METALS AND SEMICONDUCTORS IN LIQUID DIELECTRICS IN A DIRECT ELECTRIC FIELD

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When a direct electric field is applied to suspensions of metals or semiconductors in liquid dielectrics, the particles of the suspensions become aggregated and organized into peculiar structures which grow along the lines of force of the field. The process of organization of the particles ends at a definite field voltage $E \geq E_{cr}$ by the formation of a bridge which joins the electrodes and thus causes a type of breakdown of the suspensions, converting them from dielectrics into conductors or semiconductors of electricity, respectively. This process, which is of great physico-chemical interest, poses a number of questions concerning the nature of the forces which lead to the formation of a relatively stable bridge and determine its very peculiar behavior in an electric field [1-5]. All this, however, has been studied very little up to the present time. The present paper is apparently one of the first attempts at a systematic investigation of this type of phenomena.

Materials studied. Suspensions of aluminum, platinum, copper, boron carbide, and cuprous oxide were investigated. The aluminum powder used as the disperse phase was the usual "powder", the particles of which had the shape of irregular plates with maximum size of 5μ . The platinum powder consisted of globular particles $20-40\mu$ in diameter. The copper powder consisted of plates $30-40\mu$ in size. Boron carbide was the technical product with globular particles $20-30\mu$ in diameter. Cuprous oxide (chemically pure) consisted of globules $1-5\mu$ in diameter. The dispersion medium for most of the experiments was aviation gasoline (d_4^{20} 0.726; H_{boil} 47° ; k_{boil} 150°).

Suspensions in other media were also studied: in benzene (cryoscopic, twice distilled over sodium), petroleum (pure medicinal), nitrobenzene (pure), dibromhydriin (pure), and diethyl ether (purified and distilled over sodium).

The disperse phase content varied between 0.01 and 1% (by weight). Most of the experiments were carried out with suspensions containing 0.1% of the solid phase. The suspensions were not stabilized in any way.

Method of investigation. In a high voltage circuit (Figure 1) with which voltages from 300 to 4000 V could be obtained * the apparatus with the suspension (Figure 2) was connected in series with an additional resistance of 4.5 megohms (to protect the bridges from burning out). The distance between the electrodes was varied from 0.5 to 4 mm, which made it possible to set up fields of up to 80,000 V/cm. Most of the experiments were carried out at a distance of 2 mm between the electrodes. A rapidly settling suspension was sometimes agitated by blowing air through a capillary immersed in it.

An increasing voltage was applied gradually (at an approximate rate of 100 V per minute) to the electrodes of the apparatus. Readings of the galvanometer were taken at the same time. The formation of a stable bridge joining the electrodes was shown by a sharp increase of the current in the circuit, fall of potential difference, and consequent deposition of particles of the suspension from the inter-electrode space.

Behavior of Metal Suspensions in the Electric Field

Penetration of aluminum suspensions. When a direct electric field is applied to a suspension of aluminum, a movement of the particles in the latter takes place, and becomes intensified with increase of the voltage E . A clearly defined asymmetry of movement is observed. Most of the aluminum particles travel to the cathode and cover it with a more or less thick layer of loose aggregates growing toward the anode. The latter remains clean in the early stages of the process. However, in time the anode also becomes coated with particles passing over from the cathode, which form the basis of new aggregates growing toward those previously formed. Fairly often the aggregates attached to the cathode suddenly become detached and disintegrate into separate particles, giving the impression of small "explosions".

At a certain stage of the process almost the whole interelectrode space becomes filled with aggregates oriented along the lines of force of the field. Nevertheless the system still remains a dielectric.

* Voltages below 300 V were obtained from BAS-80 batteries or accumulators.

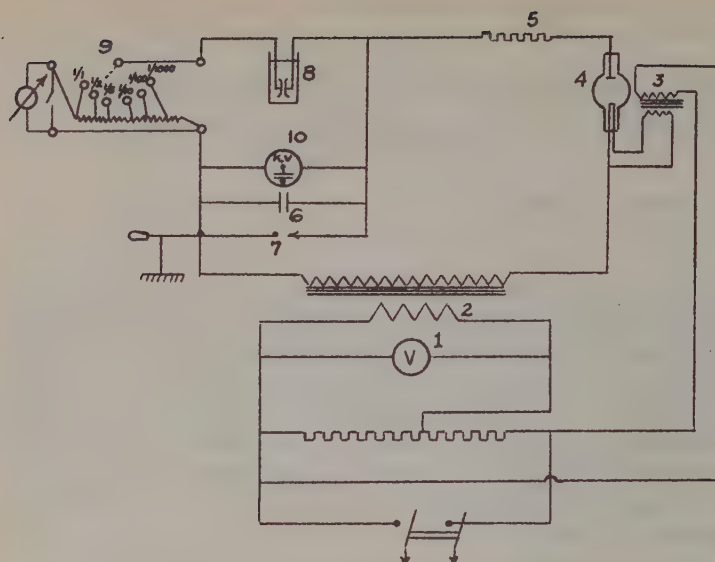


Figure 1. High voltage installation scheme: 1) Panel voltmeter; 2) step-up transformer; 3) transformer for incandescent supply; 4) keno-tron; 5) resistance of 30,000 Ω ; 6) condenser 2 μ F; 7) spark gap; 8) apparatus with suspension; 9) Ayrton shunt and 10^{-9} A galvanometer; 10) static voltmeter.

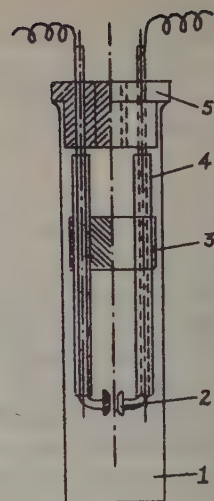


Figure 2. Apparatus for studying the effect of an electric field on suspensions: 1) Glass vessel; 2) electrodes; 3) reinforcing collar; 4) insulators; 5) cork.

However, when the field is increased to 4000 V/cm (E_{cr}), after a certain interval, which we term the induction period (usually fractions of a minute), breakdown takes place and the system becomes a conductor of electricity. This breakdown is easily shown, as already stated, by the great increase (about 10^5 times) of the current in the circuit, a fall in the field potential (from 4000 to 1 V/cm) and other effects described above.

After settling of the particles, the interelectrode space contains a single bridge, in the form of a thin thread joining the electrodes (Fig. 3). * If the walls of the apparatus are tapped, the thread (if the voltage is not disconnected) creeps along the surface of the electrodes to their lower edges; particles fall away from it in the process, and it becomes thinner and longer. If the field potential is lowered sharply, or increased, the bridge begins to move in a very peculiar way. If it is attached to the upper edge of the electrodes, the bridge inclines away from the anode, turns over, and takes up the position shown in Figure 3 b. However, the bridge remains in this position only one or two minutes and then returns. The mobility of the bridge when a current is passing through it indicates that the bond of its links between itself and the electrode surfaces is a mobile bond, which allows a certain freedom of movement. If the suspension is allowed to settle, and then the precipitate is touched with the electrodes, then when $E \geq E_{cr}$, a bridge is formed which may be withdrawn from the precipitate if the electrodes are raised carefully. Such a bridge (Figure 3 c) may reach several centimeters in length.

The electrical resistance of the aluminum bridges, determined by the "ammeter-voltmeter method" varied within fairly wide limits. The 25 bridges studied had resistances from 150 to 18000 ohms. Exceptionally, bridges were found with resistance of several megohms. However, such bridges were unstable and were quickly destroyed. The effective cross-section of bridges with resistances from 150 to 18000 ohms, calculated on the assumption that they consist of a continuous metallic thread 3 mm long, was $5.24 \cdot 10^{-9} - 4.39 \cdot 10^{-11}$ cm². This cross-section may be arbitrarily taken as the minimum area of contact between the separate structural elements of the bridge. If the high voltage supply is not disconnected, the bridges can persist for an indefinitely long time. However, they exist even after the supply is disconnected. The ability of the bridges to exist after the supply is disconnected, which we have termed "electrical memory", is the most remarkable of their properties, which makes it possible to evaluate the molecular forces to which the bridges owe their existence after removal of the field.

It was found that the electrode material (steel, aluminum, copper, lead, silver, chromium), the state of

* In good illumination this thread is visible by the naked eye.

the electrode surface, the electrode shape (disks, needles), their relative position, and the distance between them (in the limits of 0.5 to 3.5 mm) have no appreciable effect on the process of "bridge formation".

The shape of the aluminum particles also has no significant effect. Under equal conditions, bridges are formed with equal ease from plates, rods, globules, etc. The particle size, on the other hand, has a significant effect on penetration; the value of E_{Cr} increases strongly with decrease of particle size. After approximately five-fold comminution of the aluminum particles, the value of E_{Cr} rose from 4000 to 13000 V/cm.

The properties of the dispersion medium also affect the formation of bridges and their stability. Thus, increase of the viscosity of the medium increases the induction period and "electrical memory". Increased specific gravity of the dispersion medium, so that it approaches to the specific gravity of aluminum, and confers a greater kinetic stability to the suspension, shortens the induction period and prolongs the "electrical memory" of the bridges. The dielectric constant ϵ of the medium also affects E_{Cr} , which decreases with increase of ϵ .

As regards temperature, its variation between 20 and 115° did not show any influence on the value of E_{Cr} .

Mechanism of breakdown of aluminum suspensions. We will attempt to give a qualitative interpretation of the more interesting peculiarities of the mechanism of bridge formation, as far as this is possible at the present stage of the investigation. The observed asymmetry in the movement of the particles, most of which tend to move to the cathode, is caused by their low positive charge (which apparently arises as the result of contact with the dispersion medium).

The attachment of the particles to the cathode, which really commences the formation of the bridge, is the result of electrical polarization of the particles. The particles attached to the cathode are joined by others which become dipoles by electrostatic induction, and as a result are attracted to each other by their opposite poles. By this means the peculiar structures described above are formed.

One very important fact must be stressed here. The aluminum particles are coated with a thin film of non-conducting oxide, which prevents direct electrical contact between the particles and between the latter and the electrodes. Because of this the suspension remains a dielectric even when the whole interelectrode space becomes completely filled with the structures of particles and aggregates described above. In order that the suspension should be converted from a dielectric into a conductor of electricity, it is necessary to establish metallic contact between the aluminum particles and to penetrate the nonconducting films surrounding them. This conversion takes place a little after the voltage of the electric field E reaches the value E_{Cr} or E_{pen} , when breakdown of the insulating films takes place in one of the numerous aluminum chains which fill the interelectrode space, and this chain becomes a conducting metallic bridge. Hence arises a physical meaning of E_{Cr} , which should be regarded as a measure of the breakdown voltage for the nonconducting oxide films, calculated for all the links in the bridge.

Such a concept of E_{Cr} explains why the critical field voltage necessary for breakdown increases with increasing degree of dispersion of the suspension, that is, with decrease of particle size. If the oxide layer has a definite thickness, independent of particle size, then its aggregate thickness is greater as the absolute particle size is less. It follows that decrease of particle size is accompanied by a relative increase of the oxidized portion of their volume, and therefore of the total amount of the potential difference which refers to the volume of the oxidized portions.

An indirect proof of the validity of this interpretation of E_{Cr} is the fact that suspensions of noble metals, for example platinum, are converted from dielectrics into conductors at extremely low values of E (see below).

As was already noted earlier, the conducting bridge is formed at the instant of breakdown. There can be no doubt that the main role in the formation of such bridges is played by forces of electrostatic induction. However, the concluding stage in their action, which strengthens the links of the bridge, is the electrical breakdown of the nonconducting oxide films which cover these links and prevent direct metallic contact between them. What happens to the film at the moment of breakdown and how the metallic contact is effected, is not yet quite clear. Apparently, contact is achieved by a "sintering" effect, associated with diffusion of metal from one particle to another.

The process of bridge formation and analysis of its behavior provide a basis for the view that two types of bonds exist between the links. The first type of bond is electrostatic, which occurs in the stages of bridge formation preceding breakdown. The second type is metallic bonding, which arises at the moment of breakdown and because of which the bridge continues to exist even after current ceases to flow in it.

It must be supposed that the relatively high strength which the bridge possesses while the supply is connected is due to the fact that when metallic contact between the particles is broken, an electric field sufficiently strong to restore this contact is set up between the particles at the point of rupture.

Conductivity of platinum suspensions. In experiments with platinum suspensions one difficulty was met - the very rapid settling of particles. In weak fields too few particles of platinum were drawn into the interelectrode space, and as a result there was not enough material for the formation of a bridge. With strong fields, experiments with platinum carried out to determine the role of E_{cr} were inconclusive.

To overcome this difficulty, the suspension was contaminated with several minute hairs, which were intended to act as "floats" for the heavy platinum particles. Indeed, as soon as these hairs drawn in by the field, became located between the electrodes and coated with a sufficient number of platinum particles, even at low voltages such as 100 V/cm, the system was converted from a dielectric into a metallic conductor of electricity, the conductivity of which with further increase of the potential obeyed Ohm's law. In a similar experiment with aluminum suspension no such effect was observed at the same value of E . This showed that the high value of E_{cr} for aluminum suspensions is due to the necessity for breakdown of the insulating films.

It appeared of interest, however, to obtain not a "float", but a "real" bridge, built up of platinum particles only. Such a bridge was obtained in experiments with platinum powder. In contrast to the behavior of aluminum powder, which showed conductivity only when E_{cr} was reached, which had the value, as in the case of suspensions of this metal, of about 4000 V/cm, platinum powder, as was to be expected, conducted a current even at minimum values of E ; in our experiments, $E = 20$ V/cm. Evidently, mere contact between the platinum particles is sufficient for the powder to become a good conductor, as their surfaces are free from oxide films.

However, for the formation of a bridge such as is shown in Figure 3c it was necessary to set up a field of $E = 4000$ V/cm between the electrodes, and then to touch the surface of the platinum powder with them. In these conditions a bridge could be withdrawn when the electrodes were raised. Such a bridge, evidently, can be formed only by a powerful electric field, which ensures sufficient electrostatic attraction between the heavy particles of platinum when they are raised with the electrodes. In addition, when a current begins to flow through the bridge, the particles become attached to each other by forces of interatomic cohesion.

Conductivity of copper suspensions. Suspensions of copper, the oxides of which are semiconductors, occupy an intermediate position between suspensions of aluminum and platinum. When an electric field of some tens of V/cm is applied to copper suspensions (this is apparently necessary for a sufficient number of copper particles to accumulate in the interelectrode space) a weak current appears in the circuit, and steadily increases up to $E \approx 400$ V/cm. When this value of E is reached, the current increases sharply, by three or four orders of magnitude, due to the formation of a bridge of good conductivity between the electrodes. Evidently, this value of E is critical for the given suspension, and its role is to penetrate the semiconducting films of oxide on the surfaces of the copper particles.

Behavior of Suspensions of Semiconductors in the Electric Field

After a study had been made of suspensions of metals, and, in particular, a metal such as copper, the oxide film on which is a semiconductor, it appeared of interest to determine, if only in the broadest outline, the behavior of suspensions of certain semiconductors in a direct electric field.

Experiments with boron carbide suspensions. When an electric field is applied to a suspension of boron carbide in benzene, the suspended carbide particles begin to move briskly, and (at $E \approx 1000$ V/cm) a weak, apparently cataphoretic current appears, with a strength of $i \approx 5 \cdot 10^{-9}$ A.

The motion of the particles is asymmetric, but the asymmetry in the case of boron carbide is of a different sign from that of metals. The carbide particles are directed principally toward the anode, and the metallic particles toward the cathode. On receiving an overcharge at the anode, some of the carbide particles jump across from the anode to the cathode. As the value of E increases, bridges begin to form in the interelectrode space, and these are composed not of separate particles, but of fairly large aggregates of them. With further increase of E the number of such bridges increases, and this is accompanied by a steady increase of the current. If, however, the apparatus is tapped lightly, the bridges begin to crumble away, without falling to pieces. As the number of bridges decreases, the current strength falls appreciably, and rises again at the same value of E as soon as new bridges form. When the value $E \approx 3000$ V/cm (E_{cr}) is reached, the current increases sharply, by two or three orders of magnitude, to a value of $10^{-6} - 10^{-5}$ A. When the false, incomplete bridges crumble

away from the interelectrode space, a single true bridge may be seen remaining in it, stretched from electrode to electrode, which is the cause of the jump in the conductivity of the system. The shape of this bridge is somewhat peculiar; it is thin in the middle, and becomes thicker at the ends connected to the electrodes.

One peculiar effect, observed in experiments with boron carbide, should be noted — copious evolution of gas bubbles which took particles with them and generally destroyed the bridges, thus being a great hindrance to bridge formation. The nature of this gas is still not quite clear. Its evolution was not prevented when the benzene was thoroughly dried over sodium and the boron carbide was dried by prolonged heating. Possibly it was air occluded in the carbide particles (or adsorbed on them).

Boron carbide bridges have excellent "electrical memory". In favorable conditions they are capable of very prolonged existence. In our experiments they persisted for several days. Their resistance varied from tenths of a megohm to several megohms.

Experiments with cuprous oxide suspensions. When the apparatus with a suspension of cuprous oxide is connected in the circuit, the oxide particles, like particles of boron carbide, travel predominantly to the anode. As bridges begin to form in the interelectrode space, a current flows in the circuit, and this increases steadily with voltage. At the same time, suspensions of cuprous oxide showed certain peculiarities, the most striking of which was an increase of current strength with time. The higher the voltage at which the suspension was held, the more rapidly did the current increase. For example, while at 900 V the current was trebled in two minutes, at 1000 V the current strength became eighteen times as great in the same time interval. When E was increased to ~ 12000 V/cm, a small increase of current took place, and from then the current ceased to increase with time. This value of E , with regard to cuprous oxide, may also be conditionally termed E_{CR} . However, when E_{CR} is reached in the case of cuprous oxide suspensions, the fact is shown not so much by an increase of current strength — this is only approximately doubled — but by stabilization of the current. These effects are again due to the formation of a true bridge. When the particles crumble away, the bridge (a thick thread connecting the electrodes) may easily be seen with the naked eye. It has good "electrical memory" and under normal conditions persists for several days after the potential is disconnected.

The question of the nature of the above effect of current intensification with time remains unsolved at present. It is doubtful whether it is caused only by a gradual improvement of contact between the particles.

We see that the behavior of suspensions of boron carbide differs from that of cuprous oxide in a number of individual peculiarities. In the case of boron carbide at $E_{CR} \geq 3000$ V/cm a kind of breakdown takes place, whereas in the case of cuprous oxide suspensions $E_{CR} \approx 12000$ V/cm is marked mainly by a stabilization of current strength. Despite all the differences between these suspensions, however, they have in common, like suspensions of metals, the power of "bridge formation". Suspensions of all these substances in dielectrics (and also powders) become organized in a direct electric field into peculiar, ephemeral structures, which give rise at E_{CR} to a relatively stable, conducting bridge connecting the electrodes. But while the process of bridge formation in metal suspensions appears to us, in general outline, to be more or less clear, the same cannot be said concerning the analogous process in suspensions of semiconductors, which still requires more detailed investigation. A special interest is presented here by the role of E_{CR} and by the nature of the forces which bind the particles of the semiconductor in a true bridge.

SUMMARY

1. When a direct electric field is applied to suspensions of metals and semiconductors in liquid dielectrics, peculiar structures are formed from the particles and aggregates of them, disposed along the lines of force of the field. In aluminum suspensions these structures are practically nonconductors of electricity, in suspensions of copper, cuprous oxide, and boron carbide they are poor conductors, and in platinum suspensions, good conductors.

2. If the potential of the electric field E is increased, then at $E \geq E_{CR}$ a sharp increase of the electrical conductivity of the system takes place: 10^5 times in aluminum suspensions, 10^3 times in copper suspensions, and 10^2 times in boron carbide suspensions. This peculiar breakdown is accompanied by destruction of the structures described above. One thin thread, a conducting bridge of particles, remains in the interelectrode space.

3. The conducting bridges may exist in the electric field for an indefinitely long time; their resistance varies within wide limits (from tens of ohms to several megohms) and sometimes varies appreciably with time. The bridges continue to exist even if the potential is disconnected ("electrical memory").

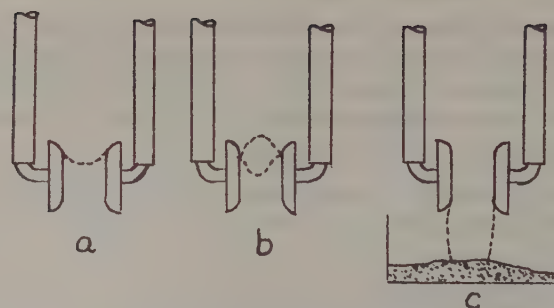


Fig. 3. Conducting bridges.

4. The time for the formation of the bridges — the induction period — and "electrical memory" increase with increase of the viscosity of the dispersion medium. Approach of the specific gravity of the particles to the specific gravity of the dispersion medium confers kinetic stability to the suspension and so favors the formation of bridges and their durability.

5. The process of bridge formation is not affected by the electrode material, the condition of the electrode surfaces, their shape (disks, needles), their relative position, or the distance between them (within the limits of 0.5-3.5 mm). The shape of the particles of the suspension is also without significance. In the case of aluminum suspensions E_{cr} is affected very strongly by particle size: E_{cr} increases with increased degree of dispersion. The value of E_{cr} depends most on the properties of the particle surfaces. If the particles are covered with non-conducting oxide film, E_{cr} is large; if such a film is absent, $E_{cr} \rightarrow 0$.

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VISCOSIMETRIC INVESTIGATIONS OF THE COAGULATION OF HYDROXIDES OF ALUMINUM AND IRON AT THE MOMENT OF THEIR FORMATION IN THE HYDROLYSIS OF SALTS

I. T. Goronovsky and A. M. Voloshinova

A large number of papers deal with the question of the coagulation of colloidal systems. However, these investigations were mainly carried out with dialyzed sols, changes in the degree of dispersion of which were effected by the action of various factors. A very small number of papers are devoted to studies of the coagulation of colloidal systems at the instant of their formation. The formation of such colloidal systems is usually observed in processes of solid phase separation from supersaturated solutions formed as the result of chemical exchange reactions. Such processes are very common in nature, and also find wide application in technology, laboratory practice, and daily life. Therefore, study of their kinetics presents great practical interest.

Theoretical bases for the study of coagulation of colloidal systems at the moment of their formation are indicated in the work of Roginsky and Todes [1], confirmed experimentally by the investigations of Lyalikov [2] and of Deryabina and Mishchenko [3]. A paper by Klyachko and Kondratyuk [4] is devoted to the role of the dispersion medium in the formation of precipitates from supersaturated solutions. Among other papers it is necessary to note the work of Matijevic and Tezak [5] who studied, on gels of silver halides, the mechanism of coagulation of hydrophobic sols at the moment of their formation.

The separation of precipitates of aluminum and iron hydroxides in the hydrolysis of their salts, studied by us, is also a typical case of the coagulation of a colloidal system at the moment of formation. This process was studied from the macroscopical aspect by Gulsky, Goronovsky, and Koganovsky [6] in a ternary system with HCO_3^- , Cl^- , and SO_4^{2-} as coagulating anions. However, only visible coagulation and sedimentation of the coagulates was studied. The present study deals with the results of a study of the mechanism of the latent coagulation of aluminum and iron hydroxides formed during hydrolysis. Viscosimetric measurements seemed to be the most appropriate for this investigation. Rabinerson [7] showed with purified sols of $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ that in such a case coagulation is accompanied by the appearance of structural viscosity as the result of coagulation structure formation. Edelman and Rebinder [8] established, in a study of the thixotropic properties of aluminum hydroxide sols with a rotational apparatus with coaxial cylinders, that aluminum hydroxide gels, formed as the result of addition of coagulant electrolytes or aluminum oxide to the sol, are elastic-viscoplastic bodies with elastic after-effects. Zuev [9] showed that by measurement of the static yield stress by the start of oscillation of steel spheres, it is possible to study the kinetics of thixotropic gelation of aluminum oxide and ferric hydroxide sols.

For our study of the kinetics of coagulation of aluminum and iron hydroxides at the moment of their formation in the hydrolysis of salts we used a modified rolling sphere viscosimeter, by means of which it was essentially possible to investigate qualitatively structure formation in these systems. The use of other apparatus for the measurements did not seem possible, as the coagulation process was very rapid.

For studying the coagulation kinetics of aluminum and iron hydroxides, the ordinary Hoesppler viscosimeter was fitted with a device developed by ourselves, by means of which it was possible to set the tube with the rolling sphere at various angles, and consequently to measure the structural viscosity using the same sphere. With the aid of this apparatus it was also possible to determine the static yield stress by Zuev's method [9]. A conventional diagram of the modified rolling sphere viscosimeter is shown in Figure 1.

To ensure that the sphere rolled in the tube in the same plane when the tube was set at different angles, the body of the viscosimeter, attached to a board with an axis, was set in a bushing placed horizontally. To this was attached a disk graduated in degrees, and a cursor with a vernier was attached to the viscosimeter axis to slide along the scale. For measurement of the limiting shear stress a graduated microscope, rotating together with the body of the viscosimeter, was attached above the viscosimeter with the aid of a small stand. A micrometer screw was used for tilting the viscosimeter as required.

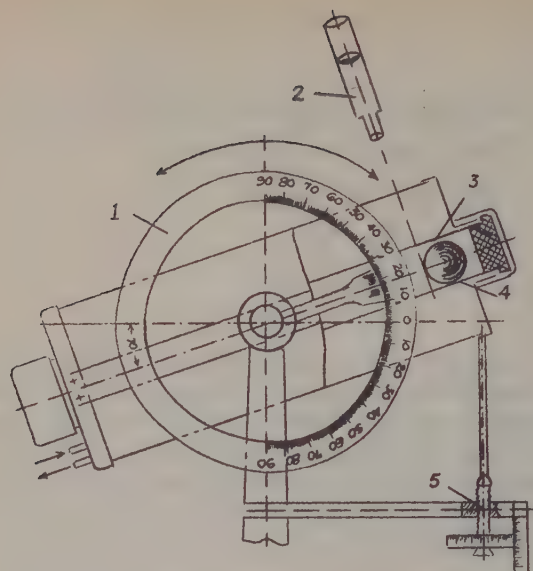


Figure 1. Rolling sphere viscosimeter: 1) Graduated scale; 2) long-focus microscope; 3) calibrated tube; 4) sphere; 5) micrometer screw.

tion parallel to the pressure axis according to the structural properties of the system. The results may conveniently be represented graphically using a coordinate scale with divisions proportional to the sine of the angle (sine scale) for the pressure axis.

In determinations of the yield stress by means of the micro-meter screw, the angle of inclination of the viscosimeter was varied steadily, and commencement of motion of the sphere was observed through the microscope. The yield stress in this case is proportional to the ratio of the acting

force (which causes the rolling) to the surface area of the sphere [9]:

$$\frac{Q \sin \alpha}{S} = \frac{1}{3} Dg \sin \alpha.$$

The following technique was used in the investigations: 100 mg/l of concentrated solutions of $Al_2(SO_4)_3$ and $FeCl_3$, were added to a solution consisting of mixtures of $NaHCO_3$ and $NaCl$ or $NaHCO_3$ and Na_2SO_4 (with a total concentration of 0.01 N). The mixture was shaken and poured into the viscosimeter, and the measurement

As the angle of inclination of the viscosimeter is varied, the component of the force due to the weight of the sphere acting in the direction in which it rolls is proportional to the sine of the angle, $P = Q \sin \alpha$ (Q is the weight of the sphere with hydrostatic correction). In the given case, for ideal liquids, the value of $1/\tau$ (τ is the time taken by the sphere to pass between the marks), which determines the rate of rolling of the sphere or the rate of flow of the liquid in the capillary gap between the tube and the sphere, is proportional to the sine of the angle of inclination of the viscosimeter

$$(\nu = k \frac{1}{\tau} = k' \sin \alpha).$$

The term P/τ , which characterizes the existence of structure formation, is in this case proportional to $\tau \sin \alpha$. As is known, this term is constant for liquids which obey Poiseuille's law, and therefore its value does not change for different angles of inclination of the viscosimeter; while for liquids with anomalous viscosity it deviates from a posi-

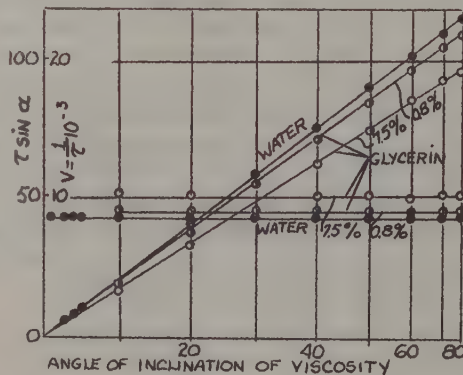


Figure 2. Calibration of rolling sphere viscosimeter (sphere diameter 15.8 mm; weight 4.98 g) at 20°.

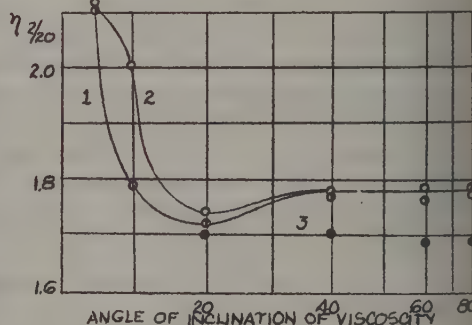


Figure 3. Change of anomalous viscosity in the coagulation of aluminum hydroxide at 2°: 1) 6 min; 2) 15 min, after addition at 100 mg $Al_2(SO_4)_3$ to the solution; 3) solution 0.004 N $NaHCO_3$ and 0.006 N Na_2SO_4 .

was carried out after a certain time interval. A new mixture was prepared for each determination. The experiments were carried out mainly at low temperatures (2°). A glass sphere 4.98 g in weight and 15.8 mm diameter was used in the measurements.

Figure 2 shows calibration data for the viscosimeter with water and dilute aqueous glycerin solution. As the graph shows, $\tau \sin \alpha$ has a constant value for these liquids at all angles of inclination. The value of $1/\tau$ for different angles of inclination of the viscosimeter is also determined by an equation to a straight line inclined to the coordinate axes if a sine scale is used.

Figures 3 and 4 show the anomalous viscosity of solutions of aluminum salts hydrolyzing under different conditions. The straight lines parallel to the abscissa axes represent the viscosities of bicarbonate - sulfate and bicarbonate - chloride solutions relative to that of water at 20° .

The anomalous viscosity curves, shown in the same Figures, clearly show the existence of coagulation structure formation during the hydrolytic separation of aluminum hydroxide. It is noteworthy that the anomalous viscosity of the colloidal system formed in a solution containing chlorides increases with time, which is evidence of the development and strengthening of coagulation structures (Figure 4). In sulfate solutions the difference between the anomalous viscosity curves is not large (Figure 3), which is explained by the stronger coagulating effect of bivalent SO_4 ions. As a result, the formation of coagulation structures is already observed in the first few minutes after addition of aluminum salts to the solution, and subsequent changes are small. It should be noted that the supermicellar structures of aluminum hydroxide gels which are formed in a sulfate medium are apparently much smaller than the supermicellar structures in a chloride medium. This may be postulated on the grounds that the upward slope of the anomalous viscosity curves in the turbulence region is much greater for chloride than for sulfate solutions. The branching of the anomalous viscosity curves in the turbulence region in the case of solutions containing chloride ions indicates that the strength and size of the coagulation structures of aluminum hydroxide in this medium varies with time. Such branching was not observed in a sulfate medium. In both solutions the process finally ended in the separation of flakes of hydroxide, visible with the naked eye, which settled out at different rates.

Figure 4 shows, in addition to anomalous viscosity curves obtained during hydrolysis of aluminum sulfate in bicarbonate - chloride solution at 2° , the anomalous viscosity curve at 20° . If the temperature change of viscosity of the solution itself is taken into account (straight lines parallel to the abscissa axis), there is no significant difference in the anomalous viscosity curves.

Figure 4 also shows the anomalous viscosity during coagulation of the same system in presence of humins (color 150, oxidizability 5.6 mg KMnO_4 per liter, temperature of the solution 2°). The position of the viscosity curves shows the increase of coagulation structure formation of aluminum hydroxide under the hydrophilizing action of adsorbed humins.

Analogous curves for anomalous viscosity were also obtained in studies of the kinetics of ferric hydroxide formation during hydrolysis of ferric chloride in bicarbonate - chloride and bicarbonate - sulfate solutions of concentrations indicated above. These investigations were carried out by the usual technique in a capillary viscosimeter connected to a manostat.

It should be noted that observations of anomalous viscosity curves alone do not permit conclusions to be drawn concerning the existence of structure formation in coagulating systems of aluminum or ferric hydroxides. Although the solutions may show anomalous viscosity, the supermicellar aggregates formed may not coalesce into

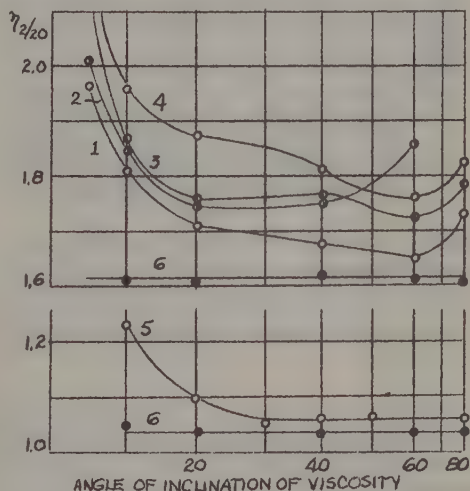


Figure 4. Effect of various factors on changes of anomalous viscosity during coagulation of aluminum hydroxide at 2° : 1) 6 min; 2) 15 min; 3) 30 min, after addition of 100 mg $\text{Al}_2(\text{SO}_4)_3$ to the solutions; 4) the same, with humins (15 min); 5) the same (6 min) at 20° ; 6) solution of 0.004 N NaHCO_3 and 0.006 N NaCl .

a single unit and exhibit elastic properties. Therefore, to characterize these systems more fully, we measured the yield stress by the technique described above, using an ebonite sphere 10.8 mm in diameter and 1.78 g in weight.

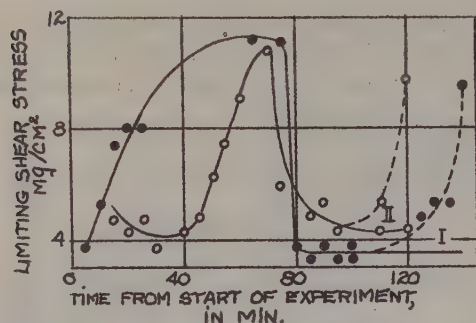


Figure 5. Variation of the yield stress with time at 2° for the systems: I - 100 mg/l $\text{Al}_2(\text{SO}_4)_3$ in a solution of 0.004 N NaHCO_3 and 0.006 N Na_2SO_4 ; II - ditto, in a solution of 0.004 N NaHCO_3 and 0.006 N NaCl .

Rebinder [8] and Zuev [9], we also carried out investigations in a rolling sphere viscosimeter, the solution not being changed before each determination. In these experiments changes of $\tau \sin \alpha$ with time were recorded at a constant inclination of the viscosimeter. Results of these measurements for aluminum sulfate and ferric chloride in bicarbonate-chloride solution are shown in Figure 6.

An important feature of these measurements is a characteristic inflexion on the $\tau \sin \alpha$ - time curves at small angles of inclination of the viscosimeter. The inflexion is apparently to be explained by the fact that latent coagulation of the hydroxides formed takes place in the initial stage, accompanied by the coagulation structure formation effects described above. In addition to the formation of primary particles as the result of supersaturation of the solution, growth of these particles takes place, leading to the formation of supermicellar structures which gives rise to an elastic system. As the degree of supersaturation decreases and the coagulation structure formation becomes complete, so the curve $\tau \sin \alpha$ - time inclines to the abscissa axis. When the structural network becomes broken and visible flakes of hydroxide are formed, indicating visible coagulation, the curve rises for the second time as the result of the resistance offered to the sphere by the flakes themselves. The inflexion point therefore corresponds to the moment when latent coagulation of the hydroxides is completed. The tangent to the curve at this point, as is known, is parallel to the abscissa axis

Figure 5 shows the results of measurements of the yield stress with time, for colloidal systems formed by the hydrolysis of aluminum sulfate in bicarbonate - sulfate and bicarbonate - chloride solutions of the type described above. The increase of the yield stress with time indicates growth of coagulation structure formation in the system, while its steep fall in the middle of the curves clearly indicates the disruption of the structure into separate aggregates, which subsequently forms flakes of aluminum hydroxide visible to the naked eye. The rise of the curves at the end indicates the apparent resistance to shear by the flakes of hydroxide settled on the sides of the tube. A characteristic feature is the rapid growth of structure in sulfate solutions and the slow growth in chloride solutions, which is fully in agreement with the anomalous viscosity curves for these systems shown above.

In view of the thixotropic properties of the systems studied, clearly demonstrated in the papers of Edelman and

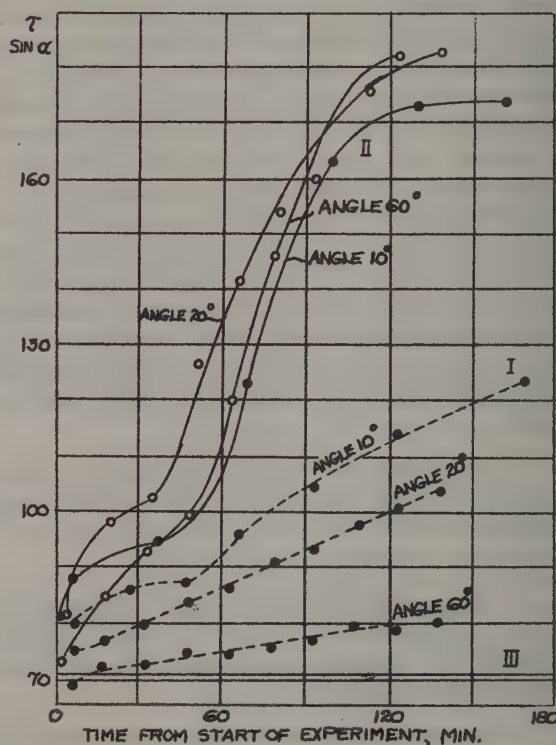


Figure 6. Variation of $\tau \sin \alpha$ with time in the coagulation of hydroxides: I - 100 mg/l $\text{Al}_2(\text{SO}_4)_3$; II - 100 mg/l FeCl_3 in a solution of 0.004 N NaHCO_3 and 0.006 N NaCl ; III - the solution.

$$\frac{d(\tau \sin \alpha)}{dt} = 0$$

This point may also be determined by the method of graphical analysis or with the aid of a mirror.

If the angle of inclination of the viscosimeter is greater than 20° , no such inflexion is observed on the $\tau \sin \alpha$ -time curves, as the structure of the system is destroyed if the rate of flow of the liquid in the capillary gap between the sphere and the tube wall is great. The difference between the steepness of the second rise of the $\tau \sin \alpha$ -time curves in the graphs for aluminum and ferric hydroxides is explained by the strength of the flakes formed. In the case of ferric hydroxide, flake formation is rapid and the flakes are large [6]. In this case the curve rises more steeply than in the case of aluminum hydroxide, which gives smaller and weaker flakes.

The results of viscosimetric investigations of coagulation kinetics of aluminum and ferric hydroxides at the moment of their formation in the hydrolysis of salts provide objective methods of investigation of the process of formation of flakes of these hydroxides under various conditions, from the instant when the solid phase is first formed to the moment when visible aggregates appear. It is particularly important that with the use of such results it is possible to study the mechanism of formation of supermicellar structures.

SUMMARY

1. The coagulation of aluminum and ferric hydroxides at the moment of their formation in the hydrolysis of salts has been studied viscosimetrically.

2. It is shown that by rheological study of the coagulation of hydroxides at the moment of their formation it is possible to investigate the mechanism of latent coagulation.

3. It is established that the latent coagulation of aluminum and ferric hydroxide at the moment of their formation in hydrolysis passes through a stage of coagulation structure formation, characterized by variation of structural viscosity with time.

4. It is shown that the static yield stress in the course of latent coagulation structure formation increases continuously up to the instant when the structural network breaks up into separate flakes visible to the naked eye.

5. It is established that with the aid of $\tau \sin \alpha$ -time curves, obtained for small angles of inclination of the rolling sphere viscosimeter, it is possible to follow the course of coagulation structure formation with time during the hydrolytic separation of aluminum and ferric hydroxides, and to determine objectively the instant when latent coagulation ends and the structure breaks up into separate flakes.

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THE CHEMICAL NATURE OF ALGINIC ACIDS

II. NATURE OF THE BOUND CARBOXYL GROUPS OF ALGIN

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Precipitates of alginic acids or, as they are commonly termed in industrial practice, algin, are formed as the result of the action of strong acids or harsh electrolysis conditions on solutions of alginates or of alginic acids. Despite the fact that algin has long been identified with alginic acids, which in turn are identified with the concept of polymannuronic acid, many workers have indicated the presence of bound carboxyl groups in algin.

Thus, Miwa, Barry and Dillon, Lucas and Stewart, and others [1, 2, 3] put forward the view that the carboxyl groups are bound in the lactone form, most probably in the 3-6 position. This supposition is quite feasible on the basis of the formula of polymannuronic acid: the formation of lactones involves the formation of a stable five-membered ring; lactones are found in plants. Lucas and Stewart confirm the presence of lactones in algin by the fact that they did not succeed in introducing more than one nitro group per monomer unit in algin. This argument is not valid, as their paper gives data for the preparation of partly more highly esterified alginic acids. It follows that their results were the consequence of competition between the direct esterification reaction with the reaction of hydrolysis of the products of complete nitration of alginic acids. This view is in agreement with the general instability of polyuronic acid esters. Thus, there are no experimental data which confirm the presence of lactones in algin.

The chemical properties of algin, described in an earlier communication [10] are also not in agreement with the hypothesis of the presence of lactones in algin. The properties of algin indicate, rather, the presence of acid anhydride linkages. On this basis we attributed to algin the formula for the incomplete anhydride of polymannuronic acid [4].

On the basis of the fact that algin is formed as the result of action of strong acids on solutions of alginic acids, and that algin does not contain the radicals of these acids but contains bound carboxyl groups, only two possibilities for the formation of algin may be postulated: formation of lactones or of acid anhydrides. From the answer to the question, which of these compounds is present in algin, it would be possible to deduce the chemical nature of algin, which has both theoretical and practical importance, as the production of alginate is based on the preparation of algin. The aim of our work was to obtain experimental confirmation of the presence or absence of lactones and acid anhydrides in algin.

EXPERIMENTAL

Algin was prepared by the technique described previously [5], but alcohol treatment was omitted. The samples of dry algin were dehydrated in a vacuum over calcium chloride, ground into a powder, and dried in a vacuum to constant weight. The other reagents were prepared by the usual methods.

To prove the presence of lactones or acid anhydrides together with free carboxyl groups, we used the difference between the action of lactones, free carboxyl groups, and acid anhydrides with alcohols and alcoholates. The latter reaction has repeatedly been used for the quantitative determination of acid anhydrides [6].

Reaction of dry algin with methyl alcohol. A weighed sample of algin powder, about 1 g, was placed in a 100 ml round flask and covered with 50 ml of absolute methyl alcohol. The contents of the flask were allowed to stand for one night, heated for one hour on a water bath under a reflux condenser, and cooled. No visible changes in the precipitate were observed in any of the experiments as the result of such treatment. After being cooled, the precipitate was filtered off and dried in a vacuum at room temperature to constant weight in a current of dry air free from carbon dioxide. The result was a powder, like algin in appearance, the yield being ~ 97% of the original sample. The product was insoluble in water, but dissolved in alkali. The methoxyl group content of the product was determined by Zeisel's method [7]; the content was 3.78 - 3.21% before hydrolysis, and methoxyl groups were absent after hydrolysis. The hydrolysis was carried out by evaporation with a small quantity of water and drying on the water bath.

Reaction of dry algin with sodium methoxide. A weighed sample of algin powder, about 1 g, was placed in a flask and covered with 10 ml of absolute methyl alcohol. The flask was allowed to stand overnight, and then a few drops of phenolphthalein in methyl alcohol was added, followed by a solution of sodium methoxide in methyl alcohol till a permanent color was obtained. No visible changes were observed in the powder. After filtration, washing with methyl alcohol, and drying, as for the previous product, a powder was obtained in a yield of about 113%, which was soluble in water and did not differ from algin in appearance.

The methoxyl group content was 1.92 - 2.1% before hydrolysis, and nil after. The hydrolysis was carried out as before.

Reaction of dry algin with concentrated ammonia solution. A weighed sample of algin, about 5 g, was gradually added to 250 ml of concentrated aqueous ammonia solution cooled with ice and stirred. The resultant thick liquid with a strong odor of ammonia was poured into ethyl alcohol. The precipitate was separated off from the alcohol, washed with alcohol till neutral to phenolphthalein, and dried in a vacuum over calcium chloride. The fibrous product was made into a powder, and the powder was dried in a vacuum to constant weight. Determinations of total nitrogen, nitrogen as ammonia, and amino nitrogen were carried out on the powder [8].

The nitrogen contents were: total, 6.02-6.00%, ammonia, 6.00-6.01%, amide, nil.

Reaction of dry algin with dry ammonia. A weighed sample of dry algin, about 5 g was placed in a U-shaped tube. The tube was cooled with a mixture of snow and salt, and dry ammonia was passed through. The reaction is accompanied by evolution of heat and water. The reaction ceased one hour after ammonia appeared at the outlet. The algin powder did not change in external appearance. The powder was treated with a stream of dry air free from carbon dioxide in a vacuum to constant weight, to remove ammonia.

The nitrogen contents were: total, 3.91-4.03%; ammonia, 3.01-2.89%; amide, 0.90-1.14%.

Quantitative determination of acid anhydrides in algin: a) by the method of Smith and Bryant [7] by titration with 0.25 N sodium methoxide and 0.25 N alkali; b) by the method of Menshutkin and Vasilyev, by titration with barium hydroxide after treatment of a weighed sample of the algin with excess of aniline. This method was used to determine anhydrides both in dry and in freshly precipitated algin [7]. The results are shown in Table 1.

TABLE 1
Carboxyl Group Content of Algin in the Form of Acid Anhydrides, as
Percentage of the Amount Titratable by Alkali

Material	Moisture (%)	Ash (%)	ml of 0.1 N NaOH solu- tion calc'd. per 1 g dry ashless algin	ml 0.1 N Ba(OH) ₂ or methoxide sol- ution calc'd per 1 g dry ashless algin	Carboxyl group content bound in the form of acid anhydrides(%)	
					Smith method	Menshutkin method
Dry algin	—	0.15	54.91	28.06	97.80	—
Dry algin	—	0.15	54.91	34.61	—	73.94
Algin gel	99.54	2.03	55.61	34.80	—	74.84

A weighed sample of algin was titrated with methoxide, then covered with 0.1 N NaOH solution in the calculated amount to neutralize the original sample. After standing (12 hours) the excess alkali was titrated with 0.1 N solution of sulfuric acid. In this case the amount of methoxide was 29.4 - 28.9 ml, and that of alkali 25.5 - 25.1 ml per 1 g algin, the total consumption being 54.4 ml. Titration with an alcoholic solution of alkali with phenolphthalein required 54.91 - 54.53 ml 0.1 N NaOH.

DISCUSSION

The results obtained in the experimental section of the work fully confirmed the supposition concerning the presence of bound carboxyl groups in algin, which was put forward on the basis of results of direct and back titration with alkali. The presence of bound carboxyl groups is indicated by the formation of esters by the action of methyl alcohol without catalysts, and by the action of alcoholic sodium methoxide solution, and also by the formation of amides by the action of dry ammonia.

From the data in the experimental section it is possible to draw a definite conclusion concerning the nature of the bound carboxyl groups. The following considerations must be taken into account. If algin contained free carboxyl groups and bound carboxyl groups in lactone form, then the reaction with alcohol and an alcoholic solution of sodium methoxide in the conditions of the experiment should result in the formation of an ester, the presence of

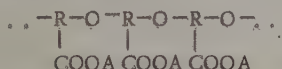
which was established experimentally, while in the reaction with concentrated aqueous ammonia solution an amide or imide should be formed, the presence of which was not established in the reaction products. Lactones should not be titrated by alcoholic alkali. On the other hand, if algin contained free carboxyl groups and bound carboxyl groups in the form of acid anhydrides, then the reaction with methyl alcohol and with aqueous methoxide solution in the conditions of the experiment should give esters, the reaction with aqueous ammonia should give ammonium salts, and the reaction with dry ammonia should give ammonium salts and amides, which were found in the reaction products.

Thus the results of the experimental section show that the bound carboxyl groups of algin are acid anhydrides. Consequently, in the chemical sense algin is an incomplete acid anhydride of alginic acids. This is confirmed by certain properties of alginic acid esters and ethers. It is known that acyl esters or simple ethers of alginic acids do not prevent precipitation of algin [3] or of alginates of polyvalent cations, but solutions of alkyl esters of alginic acids are stable both to the action of acids and of polyvalent cations [9]. It follows that the formation of precipitates of algin and of alginates of polyvalent cations takes place only on modification of the carboxyl groups. The hydroxyl groups remain unchanged.

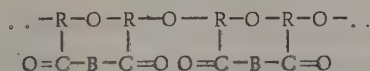
Quantitative determination of acid anhydrides showed a content of about 75% in algin gel, and 74-98% in dry algin. It is necessary to note that the results obtained are apparently a little low because the reactions take place in a heterogeneous or in an aqueous medium. In the first case the complete reaction of all the acid anhydrides with the reagent is improbable, while in the second case partial hydrolysis of amides is highly probable. In addition, the anhydride content may vary according to the conditions in which the algin was obtained.

In comparing the results of this study with the previous one [10] it is necessary to note that the formation of algin by the action of acids on alginate solutions proceeds through the formation of alginic acids. This scheme for the formation of algin explains the need for an excess of precipitating acid in comparison with the amount of acid necessary for double decomposition. The equilibrium nature of the reaction makes it possible to find the cause of the presence of ash in algin and the cause of algin losses in washing, and also makes it possible to indicate methods of decreasing losses of algin in the form of alginic acid solutions.

It must be noted that the solubility rule for alginic acid derivatives, formulated previously [4], has attained wide generalization. Alginic acid derivatives with the structure:



are soluble in water to form viscous colloidal solutions. Here \underline{R} is a mannuronic acid residue, and \underline{A} is a univalent atom or group of atoms (hydrogen, metal, alkyl radical, amide group, etc.). Alginic acid derivatives with the structure:



are insoluble in water. Here \underline{R} is again a mannuronic acid residue, and \underline{B} is some bivalent atom or bivalent group of atoms (oxygen, residue of a bivalent metal base, imide groups, etc.). Because of the presence of a considerable number of carboxyl groups (100 - 1000) in the alginic acid molecules, in addition to the above types, a number of intermediate types of compounds are possible (incomplete alginates, incomplete anhydrides, incomplete esters, etc.). It is therefore possible to obtain a whole series of compounds of graded solubility in water. The transition from water-soluble to insoluble compounds is accompanied by an unlimited increase of the solution viscosity up to complete loss of flow, that is, up to the formation of a gel. This property of intermediate compounds may be utilized for increasing the viscosity of aqueous solutions of alginates, esters, and other derivatives of alginic acids.

In conclusion, we present a comparison of certain properties of alginic acids and their incomplete alginates (algins), by means of which these substances may be distinguished (see Table 2).

SUMMARY

1. The reactions of dry algin with methyl alcohol, sodium methoxide, and dry ammonia were studied. The acid anhydride content of algin was quantitatively determined.

2. The precipitates of alginic acids formed by the action of acids on solutions of alginates or alginic acids, or by the electrolysis of these solutions are incomplete acid anhydrides of alginic acids.

TABLE 2

Properties of Alginic Acids and Algin

Property	Alginic acids	Algin
Solubility in water	Soluble	Insoluble
Reaction with alkalies	Form soluble alginates only	Forms soluble and insoluble alginates
Reaction with acids, without heat	Form a precipitate of algin	Does not react
Reaction with aqueous solutions of barium and calcium hydroxide	Form insoluble and water-soluble alginates	Forms insoluble alginates only
Reaction with alcohol	Precipitation of alginic acids, precipitate soluble in water	Dehydration and formation of esters
Reaction with dry ammonia	Form ammonium salts	Forms salts of amido-acids

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* See Consultants Bureau Translation, page 285.

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THE STRUCTURE OF GELS

VI. PREPARATION OF GELS AND GLOBULAR STRUCTURES FROM RUBBERS BY VULCANIZATION OF SOLUTIONS

P. I. Zubov, Z. N. Zhurkina, and V. A. Kargin

This paper presents experimental material on the properties of gels and globular structures obtained from natural (smoked sheet) and synthetic (butadiene) rubbers. The principal reason for the study was the necessity of developing a method of evaluating the molecular structure of different rubbers. The solution of this problem is of great practical significance, as many properties of rubbers are determined by the nature of their molecular structure.

In our studies of the mechanism of formation of protein gels [1] it was shown that during deformation, gels exhibit various relaxational properties according to the concentration. Larger mechanical losses are found in concentrated than in dilute gels. It may be supposed, however, that relaxation processes depend not only on the concentration but also on the molecular structure of the gel-forming substance. In particular, gels prepared from branched polymers should have a greater selection of relaxation periods than gels prepared from linear polymers.

Gels of rubber were prepared by vulcanization, at room temperature, of 20% toluene solutions of the rubbers with sulfur monochloride (3% on the weight of the rubber). Before solution, the rubbers were masticated for about 5 minutes on cold rolls. The toluene was previously dried over calcium chloride and distilled; the sulfur monochloride was saturated with sulfur and distilled over excess sulfur. 4% solution of sulfur monochloride in toluene was used for the preparation of the gels.

After addition of sulfur monochloride solution to the rubber solution, the mixture was thoroughly stirred

and poured into aluminum beakers, in which the mechanical tests on the gels were carried out (usually on the day after preparation). To prevent evaporation, the beakers with the gels were placed in basins containing glycerin and covered with glass lids before testing. For the same reason glycerin was added to the beakers containing the gels in measurements of deformation carried out at temperatures above 25°.

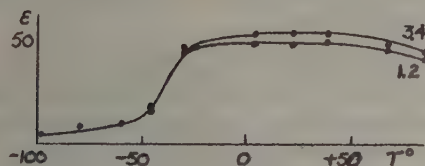


Fig. 1. Deformation of natural rubber gels; measured at frequencies: 1 - 1000; 2 - 100; 3 - 10; 4 - 1 oscillation per minute.

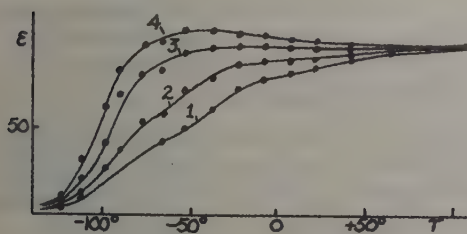


Fig. 2. Deformation of synthetic rubber gels; measured at frequencies: 1 - 1000; 2 - 100; 3 - 10; 4 - 1 oscillation per minute.

The mechanical properties of rubber gels, were determined by means of the Aleksandrov-Gaev frequency apparatus, as previously in the case of gelatine gels [1].

Figures 1 and 2 show data on the temperature dependence of gels of natural and synthetic rubber. It is seen from these Figures that deformation of natural rubber gel begins to develop at about -50°, as the temperature rises, the deformation increases rapidly irrespective of the rate of the deforming force; at -30° the deformation reaches a maximum value, which remains practically constant up to 100°.

The absence of elasticity in natural rubber gels at temperatures below -50° is apparently due to crystallization of the rubber. The sharp ascent of the deformation - temperature curve at about -50° is associated with melting of the rubber and transition of the system into the high-elastic state. Consequently, natural rubber gels behave in the same ways as dilute gels of gelatin tanned with quinone, the behavior being practically independent of the frequency throughout the temperature range.

A different state of affairs is found in the deformation of a gel prepared from SK-B (butadiene) synthetic rubber solution. The deformation in this gel begins to develop at about -100° . A clearly defined relaxational character is shown by the deformation. As the temperature rises, the dependence of the magnitude of deformation on the frequency of deformation at first increase, and then decreases. At temperatures about 50° almost complete degeneration of large periods of relaxation takes place. This type of gel deformation is apparently due to the branched nature of the SK-B macromolecules. Thus, on the basis of a study of the mechanical properties of gels it is possible to evaluate differences in the structure of the molecules of natural and synthetic rubber. Branching of the polymer molecules should not affect the nature of the intermolecular action only. This feature of macromolecular structure should also be manifested in intramolecular actions, that is, in the formation of globular structures. A linear or branched structure of the molecules should affect the specific volume and shape of the globules formed.

To verify this supposition, experiments were carried out on the preparation of globular structures from natural and synthetic rubber. The degree of globulization was determined by measurements of the viscosity of the rubber solutions during vulcanization.

In contrast to proteins [2], the intramolecular action leading to the formation of globular structures was produced, in the case of rubber, by vulcanization of 0.16% toluene solutions of natural and synthetic rubber at 95° with sulfur monochloride. The toluene and sulfur monochloride were purified in the same way as for the preparation of gels. The kinetics of formation of globular structures, and the dependence of the viscosity of solutions of globular rubbers on the concentration, were studied. The effect of the amount of sulfur monochloride and of the molecular weight of natural rubber on the globulization process was also elucidated.* To determine the dependence of viscosity on concentration, solutions of globular rubber were concentrated in a vacuum at $40-45^{\circ}$, and the viscosity was then measured at different dilutions.

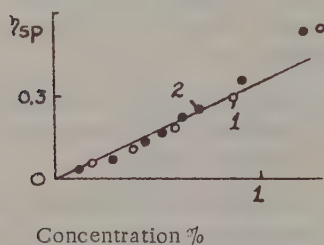


Fig. 4. Dependence of the viscosity of globular rubbers on concentration: 1) Natural rubber, low degree of mastication + 500% S_2Cl_2 ; 2) natural rubber; highly masticated + 500% S_2Cl_2 .

viscosity; the limiting value of the viscosity depends neither on the molecular weight of the rubber nor on the amount of sulfur monochloride, which is evidence that the globules formed from natural rubber have the same specific volume. For solutions of synthetic rubber under analogous conditions, higher values of viscosity are obtained, due apparently to looser packing of the globules.

In the case of synthetic rubber the limiting value of viscosity is established after a longer interval of time. It is seen from Figure 5 that a fall of viscosity takes place also when solutions of natural rubber which do not contain sulfur monochloride are heated. In this case the decrease of viscosity is caused by the degradation of the

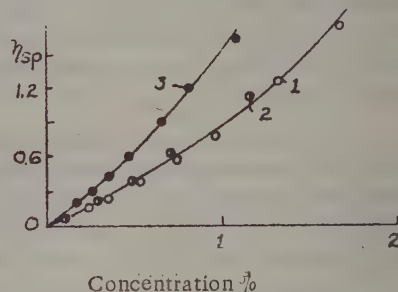


Fig. 3. Dependence of the viscosity of solutions of globular rubbers, low degree of mastication, on the concentration: 1) Natural rubber + 500% S_2Cl_2 ; 2) natural rubber + 50% S_2Cl_2 ; 3) SK-B + 500% S_2Cl_2 .

As is seen from Figures 3 and 4, natural rubber solutions, regardless of the molecular weight of the original rubber and of the amount of sulfur monochloride, show a linear dependence of viscosity on concentration up to $\approx 1\%$ concentration, and SK-B solutions up to 0.4% . These results may be explained by the fact that the globules formed from the flexible linear molecules of natural rubber are closer in shape to spherical particles than are the globules of SK-B.

The kinetics of formation of globular systems was studied as follows: after the viscosity of the original solution had been measured, 20% solution of sulfur monochloride in toluene was added to it, and the viscosity of the mixture was measured after thorough stirring. The solution was then heated to 95° and its viscosity measured at regular intervals. The heating of the solution was continued until a definite value of the viscosity was established.

The data in Figures 5 and 6 show that the addition of sulfur monochloride to natural rubber solutions causes a sharp fall of vis-

* Natural rubber of different molecular weights was obtained by variation of the time of mastication.

natural rubber molecules as the result of the action of atmospheric oxygen.

Experiments were carried out in absence of air, to exclude the action of oxygen. For this purpose viscosimeters were prepared with the aid of which it was possible to study the kinetics of formation of globular structures of rubbers in complete absence of air. A diagram of the vacuum viscosimeter is shown in Figure 7.

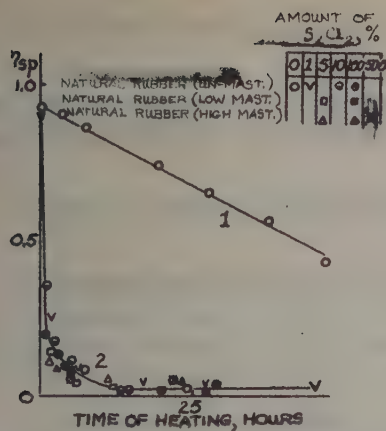


Fig. 5. Kinetics of globulization of natural rubber solution in presence of from 1 to 500% S_2Cl_2 (2), and variation of the solution viscosity in absence of S_2Cl_2 (1).

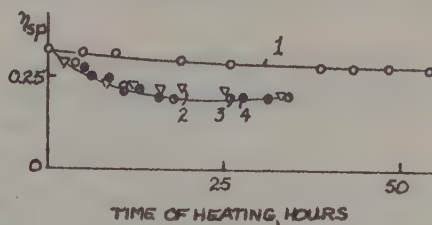


Fig. 6. Kinetics of globulization of SK-B solutions in presence of S_2Cl_2 : 2) 1%, 3) 10%, 4) 100%, and variation of the solution viscosity in absence of S_2Cl_2 (1).

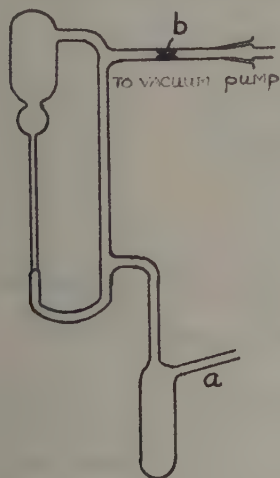


Fig. 7. Diagram of the vacuum viscosimeter.

The experimental procedure with the vacuum viscosimeters was as follows: the solution of rubber and a solution of sulfur monochloride were poured into the viscosimeter ampoule through the side-tube a (10% S_2Cl_2 on the weight of the rubber). The side-tube was then sealed off and the air removed with the aid of a high-vacuum pump and with repeated freezing of the solution in liquid nitrogen alternating with melting. The viscosimeter was then cut off from the pump by sealing the connection b, and transferred to a thermostat for viscosity measurement. The first measurement of viscosity was carried out before heating, and subsequent determinations after heating at 95°.

Figure 8 shows data on viscosity changes of solutions of natural and SK-B rubber with and without additions of S_2Cl_2 for different times of heating at 95° in presence and absence of air. It is seen from these data that sulfur monochloride causes a decrease in the viscosity of natural rubber solutions both in presence and in absence of air. The greater fall of the viscosity of natural rubber solutions in presence of air and sulfur monochloride is apparently due not only to globulization but also to the degradation of the molecules of natural rubber by the action of atmospheric oxygen.

In solutions of SK-B the decrease of viscosity during vulcanization in air is very small, and is completely absent after removal of air. On the basis of these data it may be concluded that intramolecular action (globulization of the molecules) does not take place in solutions of synthetic rubbers.

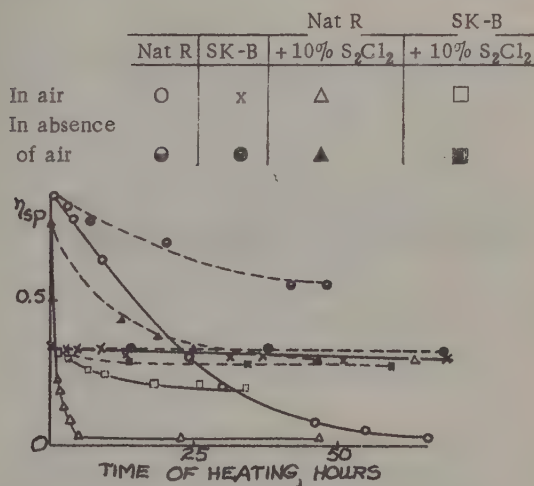


Fig. 8. Kinetics of globulization of rubber solutions.

SUMMARY

1. The mechanical properties of gels prepared from solutions of natural and synthetic rubber have been studied.
2. It is established that gels of synthetic rubber (SK-B) have a wide selection of relaxation periods. Gels of natural rubber (smoked sheet) behave as ideally elastic bodies, and obey Hooke's law under 1000-fold changes of the rate of deformation.
3. The viscosity of dilute solutions of natural rubber and SK-B in presence of sulfur monochloride has been studied.
4. It was found that S_2Cl_2 sharply lowers the viscosity of solutions of natural rubber and has hardly any effect on the viscosity of solutions of synthetic rubber.

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* See Consultants Bureau Translation, page 185.

INVESTIGATION OF THE STRUCTURAL-MECHANICAL PROPERTIES OF CONCENTRATED AQUEOUS SUSPENSIONS OF CEMENT IN THE SETTING PROCESS

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The structure of cement paste, in contrast to the structure of other disperse colloidal systems, has the property of becoming stronger with time. This peculiarity of cement pastes makes impossible the application of existing instruments and methods to the study of its structural-mechanical properties. It was necessary to develop a technique in which strengthening of the structure would not affect the results of measurements.

A technique for investigating the structural-mechanical properties of cement paste in the process of structure formation was developed with the aid of an electronic Selsyn apparatus, based on the principle of pure shear in the space between two coaxial cylinders. A general view of the apparatus is shown in Figure 1.

The period of action of the load was reduced to the minimum: 1-3 seconds, that is, the time in the course of which the structure of cement paste remains practically unchanged. A complete curve for the deformation kinetics in this short interval could be obtained as the result of automatic recording of the process: of the deformation kinetics, magnitude of the applied force, and time.

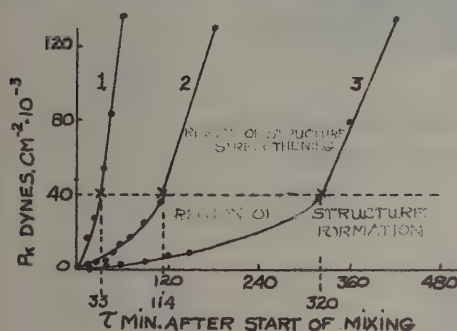


Fig. 3. Variation of the flow limit with time from the start of mixing of cement paste of high-alumina cement: 1) $W/c = 0.28$; $\Delta P_k / \Delta \tau = 2800$; 2) $W/c = 0.40$; $\Delta P_k / \Delta \tau = 1370$; 3) $W/c = 0.50$; $\Delta P_k / \Delta \tau = 1000$ dyne \cdot cm $^{-2}$ per min.

depending on the shearing surface of the cylinder: from 50 to $50 \cdot 10^4$ dynes/cm 2 .

In rapid measurements with instantaneous application of a constant load it was found that the high-elastic modulus E_1 and the elasticity modulus E_2 cannot be taken as absolute constants which characterize the system, as in a number of cases it is not possible to separate instantaneous and elastic deformations. Moreover, in such short intervals of time high-elastic deformation has no time to develop completely. Therefore, characterization of the system by its complete modulus also becomes meaningless, as the modulus does not reach an equilibrium value.

Thus, of the five constants: P_k , E_1 , E_2 , η_1 and η_2 , which are commonly used to characterize the structural-mechanical properties of undestroyed disperse and colloidal systems [1 - 3], in the case of cement paste we are left with P_k and η_1 (the elastic viscosity η_2 cannot be calculated, as it proves impossible to determine the velocity gradient because the instantaneous deformation ϵ_0 is not constant). These constants characterize the most practically important properties of cement paste - strength and creep, and provide sufficiently full information on its structural-mechanical properties.

Cements with different contents of aluminates were studied, as these components have the greatest effect

The stressed state in the material is produced by the application of a torque, set up by twisting of an "electric roller" between two Selsyns through an angle proportional to the torque. The magnitude of the torque is determined by the amplitude of oscillation of the loop, an oscillograph, and is recorded, like the curve for the deformation kinetics and the time, on sensitized paper (Figure 2). The deformation kinetics was recorded by a photoelectric device, the purpose of which was to amplify the shearing deformation and convey it to the oscillograph loop. The accuracy of measurement of the absolute deformation is 1.2 - 2.4μ (depending on the radius of the inner cylinder) for 1 mm ascent of the deformation curve on the oscillogram.

The time is recorded in seconds in the form of separate strokes, the length of which depends on the speed of the sensitized paper, and varies from 1.5 to 90 mm. The absolute values of the applied torque in the apparatus vary from 100 to 2500 g \cdot cm, and the stresses may vary over a wide range

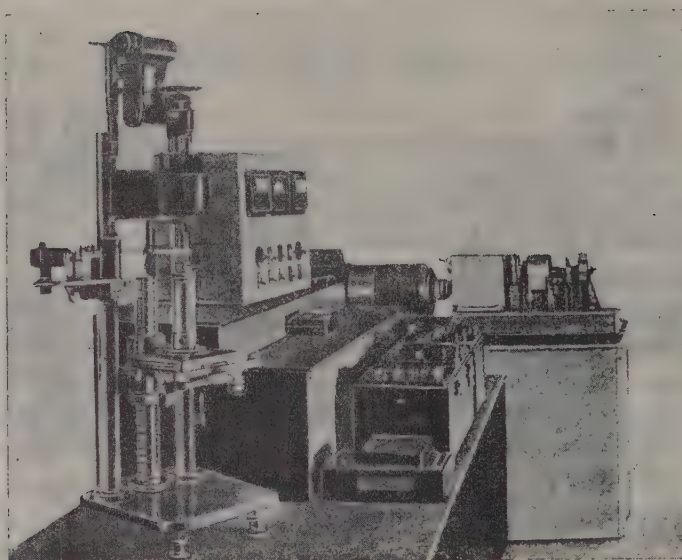


Fig. 1. General view of electronic selsyn apparatus for the investigation of structural-mechanical properties of elastico-plastic systems.

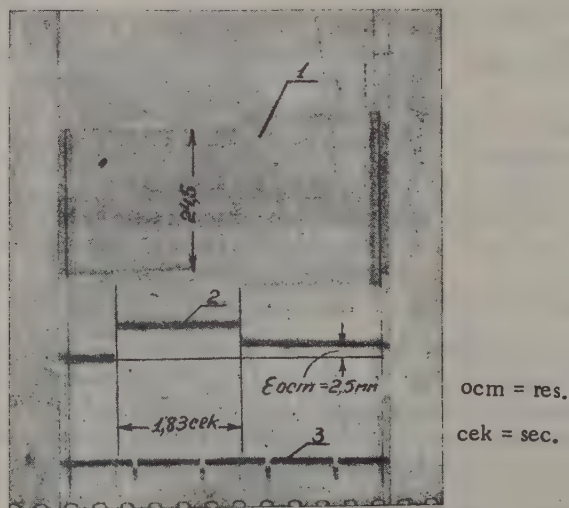


Fig. 2. Oscillograph trace showing the torque, curve for the deformation kinetics, and time.

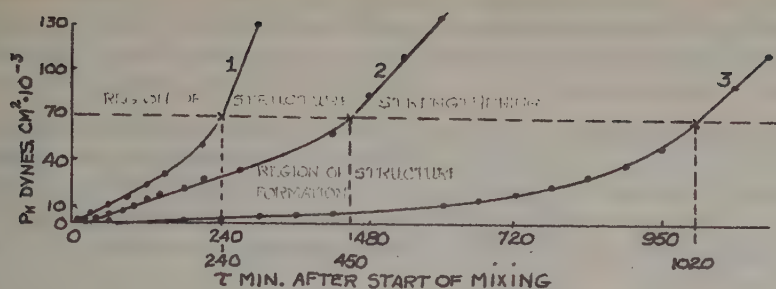


Fig. 4. Variation of the flow limit with time from the start of mixing of cement paste of low-alumina cement: 1) $W/c = 0.28$; $\Delta P_K/\Delta \tau = 1000$; 2) $W/c = 0.40$; $\Delta P_K/\Delta \tau = 440$; 3) $W/c = 0.50$; $\Delta P_K/\Delta \tau = 380$ dyne. cm^{-2} per min.

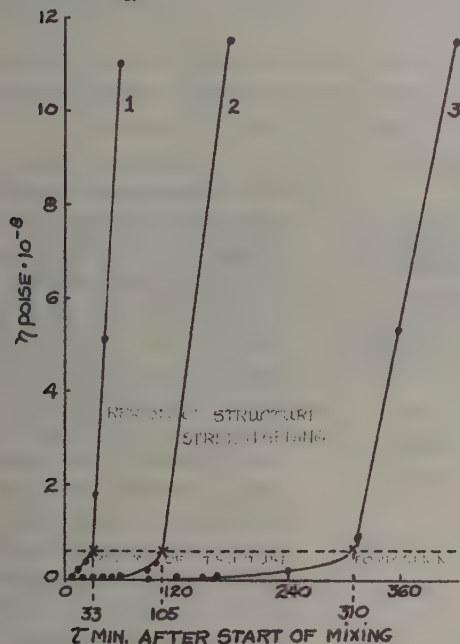


Fig. 5. Variation of the maximum plastic viscosity with time from the start of mixing of high-alumina cement: 1) $W/c = 0.28$; $\Delta \eta/\Delta \tau = 0.3 \cdot 10^8$; 2) $W/c = 0.40$; $\Delta \eta/\Delta \tau = 0.15 \cdot 10^8$; 3) $W/c = 0.50$; $\Delta \eta/\Delta \tau = 0.103 \cdot 10^8$ poise/min.

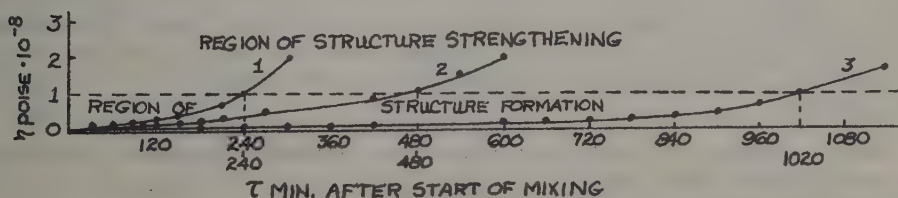


Fig. 6. Variation of the maximum plastic viscosity with time from the start of mixing of low-alumina cement: 1) $W/c = 0.28$; $\Delta \eta/\Delta \tau = 0.017 \cdot 10^8$; 2) $W/c = 0.40$; $\Delta \eta/\Delta \tau = 0.0085 \cdot 10^8$; 3) $W/c = 0.50$; $\Delta \eta/\Delta \tau = 0.006 \cdot 10^8$ poise/min.

on the rate of setting of cement paste: high-alumina cement from the "Gigant" factory with a content of 13.5% of tricalcium aluminate, and low-alumina cement from the "Komsomolets" factory with a content of 5.3% tricalcium aluminate, with water-cement ratios of 0.28, 0.40, and 0.50. The curves for the deformation kinetics $\epsilon(\tau)$ of cement pastes were plotted for different time intervals from the start of mixing. The applied stress was increased with strengthening of the structure, but was kept constant all the time while the deformation kinetics data were obtained up to unloading (2-3 sec). The cement paste was mixed by the standard method in the quantity required to fill simultaneously several beakers with different shearing surfaces: 400, 180, 90, 30 and 20 cm^2 . The measurements were started with the large beakers, and these were replaced by progressively smaller ones as the structure became stronger, as greater loads were required for shear.

From the curves of deformation kinetics for each time interval from the start of mixing, the rate of flow $d\epsilon/d\tau$ was determined after removal of load, where ϵ is the

relative deformation, and τ is the time the system was under load. From the graph for the dependence of the rate of flow on the applied stress, the limit of flow (elastic limit) was determined for different times from the start of mixing of two cements for three water-cement ratios. It is seen that the flow limit of both cements increases with increased time from the start of mixing.

The character of the growth of the flow limit P_k is seen from Figures 3 and 4. A slow rise of the curve is seen at first, and after some time the curve becomes a straight line, which indicates a rapid increase of the flow limit at a constant rate of increase. The transition of the curve into a straight line for the two cements takes place at different times from the start of mixing and at different values of the flow limit. However, for different ratios of water to cement for the same cement the limit of flow retains the same value, and only the time of transition to a straight line changes.

The maximum plastic viscosity, defined as $\eta = (P - P_k) / (d\epsilon/d\tau)$, also rises slowly at first. Its rapid increase begins after the same intervals from the start of mixing as the limits of flow (Figs. 5 and 6).

This course of the $P_k(\tau)$ and $\eta(\tau)$ curves shows that the character of the increase of the strength of the structure changes sharply after some time from the start of mixing. The flow limit and the maximum plastic viscosity attain a constant rate of increase and their values increase considerably. This transition from one condition of a plastic liquid-like mass with a low value of flow limit and of maximum plastic viscosity, into another condition, when the cement paste begins to lose plasticity and begins to acquire strength, expressed by an increase of the flow limit and of the maximum plastic viscosity, does not occur at once.

Limit of Resistance to Uniaxial Compression (kg/cm^2) of Specimens Made from Cement Paste

Times of storage of specimens, days	Immediately after mixing	Disruption of structure in the region of			
		Formation, time after start of mixing		Strengthening, time after start of mixing	
		125 min.	200 min.	305 min.	425 min.

High-alumina cement, $W/c = 0.50$

3	290	—	275	—	150
7	340	—	360	—	137
28	450	—	475	—	240

Low-alumina cement, $W/c = 0.28$

3	320	300	—	100	—
7	700	740	—	330	—
28	900	875	—	390	—

The region of the curve before it passes into a straight line determines the period of structure formation in which the creation of a coagulation structure predominates. In this region, in our view, the structure of the cement paste is formed in some way depending on the conditions in which the process takes place. Its disruption, followed by thixotropic restoration, is possible here. After the transition to a straight line the region of structure strengthening commences, where crystallization processes predominate, in consequence of which the flow limit and the maximum plastic viscosity increase.

Disruption of the structure in this region leads to irreversible processes, which indicates the presence of a brittle-elastic body in the system. Uniaxial compression tests on specimens made from cement paste with disrupted structure in the formation region and in the strengthening region showed that disruption of the structure in the formation region has no effect on the strength of the specimens, but disruption of structure in the strengthening region lowered their strength considerably (see Table).

Analysis of the $P_k(\tau)$ and $\eta(\tau)$ curves showed that P_k and η in the structure formation process are inter-related values. The fact that the $P_k(\eta)$ curves coincide for $W/c = 0.28, 0.40$, and 0.50 shows that their course is independent of the water-cement ratio (Figure 7). It is seen from Figure 7 that in the first period after the start of mixing, that is, in the formation region, the rate of growth of the flow limit is greater than in the region of structure strengthening. The rate of increase of plastic viscosity, on the other hand, increases in the region of structure strengthening.

As is seen from Figure 5, the plasticity of cement paste, its pliability, depends on the relation between the flow limit and the maximum plastic viscosity [4]. The greater is this ratio, the more plastic is the cement paste at a given time after the start of mixing.

However, the plasticity of cement paste should be evaluated mainly in terms of the time for which it retains the plastic state, as the high value of the ratio P_k/η in the first few moments after the start of mixing

falls rapidly during the first tens of minutes. This is found for rapidly setting cements. Thus, it is seen from Figure 8 that cement paste from high-alumina cement at the moment of mixing is more plastic than paste from low-alumina cement (Figure 9). However, the plasticity of paste from high-alumina cement falls rapidly, while paste from low-alumina cement remains plastic for a long time.

With the aid of $\underline{P}_k(\eta)$ curves it is possible to select a cement or to bring it to a required state of plasticity with various additions. The logarithmic dependence between these two constants is expressed by a straight line with a tangent of its angle of inclination \underline{A} , which characterizes the plasticity of a given cement. For paste from high-alumina cement the constant \underline{A} has the value of 0.62, for low-alumina cement, $\underline{A} = 0.94$.

By means of studies of the structural-mechanical properties of cement paste in the setting process it proved possible to elucidate the nature of changes of these properties, to obtain new quantitative characteristics for them, and also to formulate views on the mechanism of structure formation. These views, which agree with those developed by Rebinder [5, 6] describe the interaction of cement grains with water, accompanied by chemical and adsorptional peptization of the solid phase.

From the moment when water is added to the cement powder and throughout the whole period of structure formation, the adsorptional layers of water penetrate into the microcrevices and assist the mechanical destruction of cement particles, which is intensified by chemical peptization, which produces destruction of the cement particles as the result of hydration reactions. During this period formation of coagulation structure, which confers plasticity to the cement paste, predominates. Increase of the surface of the solid phase per unit volume leads to an increase of the hydration rate, and also to a decrease of the distance between the particles, and consequently, to an increase of the molecular bonds between them. Gradually hydrates, the result of hydration, begin to grow on the surfaces of the broken cement grains. The particles of the solid phase are already surrounded not by water, but by solutions of these hydrates, supersaturated with respect to the larger crystals. The products of the hydration reactions begin to crystallize out, the system passes into the stage of structure strengthening, in which processes of crystallizational hardening take place. These are the phenomena responsible for the sharp increase of the flow limit and maximum plastic viscosity, which confers the properties of a brittle-elastic body to cement paste.

Due to the adopted method of calculating the undestroyed structure as plastic, that is, from the excess of the acting stress over the flow limit, it was possible to establish an interrelationship between such important structural-mechanical properties as the flow limit \underline{P}_k and the maximum plastic viscosity η_1 , which could not have been done if the

viscosity of the undestroyed structure were calculated as the effective viscosity, that is, from the acting stress, as in this case the value of the viscosity would decrease.

SUMMARY

1. Two objective constants have been established — the limit of flow (elasticity) \underline{P}_k , and the maximum plastic viscosity η , which characterize the elastic-viscoplastic properties of cement paste, and also the kinetics of structure formation during setting and initial hardening.

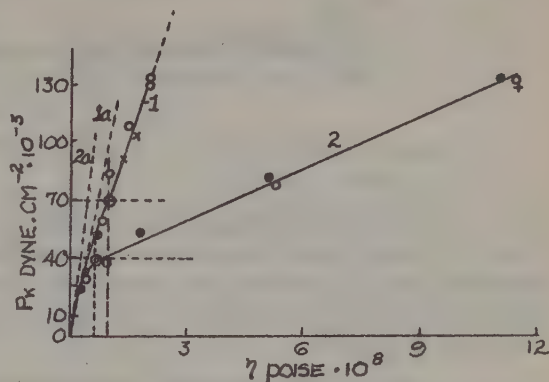


Figure 7. Relationship between \underline{P}_k and η in the structure formation process of cement: 1) low alumina, $\Delta \underline{P}_k / \Delta \eta = 103 \cdot 10^{-3}$ (1a) in the formation region and $\Delta \underline{P}_k / \Delta \eta = 0.62 \cdot 10^{-3}$ in the structure strengthening region; 2) high alumina, $\Delta \underline{P}_k / \Delta \eta = 1.7 \cdot 10^{-2}$ (2a) and $0.085 \cdot 10^{-3}$ in the respective regions.

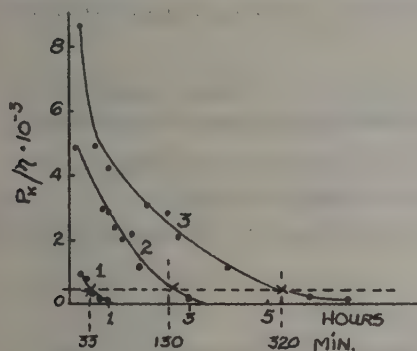


Figure 8. Variation of \underline{P}_k/η with time from the start of mixing for high-alumina cement at W/c ratios: 1) 0.28; 2) 0.40; 3) 0.50.

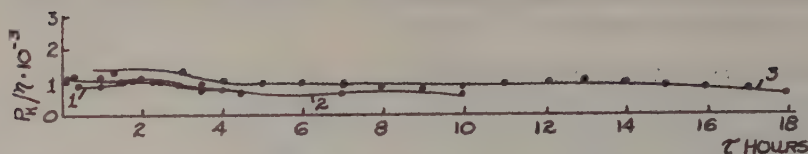


Figure 9. Variation of P_k/η with time from the start of mixing for high-alumina cement at W/c ratios: 1) 0.28; 2) 0.40; 3) 0.50.

2. It is shown that the plasticity coefficient P_k/η proposed by M. P. Volarovich may be used for characterization of plastic cement paste. However, the plasticity of cement paste should be characterized not only by the value of P_k/η , but also by the period of retention of the plastic state during structure formation. Thus, paste from high-alumina cement loses plasticity more rapidly during the process of structure formation than does paste from low aluminate cement.

3. A quantitative relationship between structure formation processes and the water-cement ratio is shown for both cements.

4. Two stages of structure formation in the process of setting and the start of hardening of cement paste have been established: a) formation of structure, and b) strengthening of structure.

The formation stage is characterized by the predominance of formation of a coagulation thixotropic structure which is reversibly restored on disruption, and the strengthening stage, by a crystallization structure with the properties of a brittle-elastic body.

5. It is shown that the coagulation structure of paste from high-alumina cement is almost twice as strong as that from low-aluminate cement, which may be explained on the view that in the first case hydroaluminates predominate, with weaker bonds in the formation of a coagulation spatial network than those possessed by hydro-silicates.

6. A relationship between the constants P_k and η , independent of the water-cement ratio, has been established for each cement of different mineralogical composition. \underline{A} is the tangent of the angle of inclination, and $\frac{\Delta \log P_k}{\Delta \log \eta}$ is a constant for the cement, which characterizes the ability of the cement to form plastic mixtures on mixing with water, that is, the "plasticity" of the cement.

7. These investigations support the concepts developed by Academician P. A. Rebinder concerning the formation of a coagulation-crystallization structure during mixing and beginning of setting of cement paste.

8. The calculation of viscosity of the undisrupted structure of a quasi-solid system as plastic viscosity, from the excess of the acting force over the flow limit, has been shown to be valid in practice.

The authors express their gratitude to Academician P. A. Rebinder for valuable advice in the course of these investigations.

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GELATINIZED EMULSIONS

XI. EMULSIONS OF THE W/O TYPE OF MAXIMUM CONCENTRATION, STABILIZED BY ALKALI OLEATES

L. Ya. Kremnev and N. I. Kuibina

Emulsifiers are usually classified as hydrophilic and oleophilic, in relation to their capacity for stabilization of direct and reverse emulsions. Indeed, when an emulsion is composed of two pure liquids (a case which does not often occur in practice) alkali soaps, which are hydrophilic and have good solubility in water, favor the formation of emulsions of the o/w type. However, if the properties of water are changed by the solution of a sufficient amount of a salt with a univalent cation, phase reversal in the direct emulsion and stabilization of the reverse emulsion take place [1].

We showed previously that when 0.25 mole NaCl is added to an aqueous solution of sodium oleate, stabilization of highly concentrated emulsions of the o/w type still takes place, but with a considerably decreased content of dispersed benzene in 1 ml of the soap solution [2]. Further increase of salt concentration stops the formation of direct emulsions. Other salts act similarly. The possibility of stabilization of limiting emulsions of maximum concentration in presence of large concentrations of electrolyte was not examined in the paper cited.

The present paper reports the conditions and results of stabilization of highly concentrated emulsions of the w/o type with the aid of alkali oleates in presence of sufficient amounts of univalent cations.

When a considerable amount of salt is present in a soap solution, very dense coagulates of soap appear at the separation boundary of the liquids, which hinder emulsification considerably. Therefore, highly concentrated emulsions of the w/o type were obtained by a method which differed somewhat from that used by us previously [3]. A certain amount of oleic acid was dissolved in benzene, and a limited volume of the benzene solution (0.3 - 0.5 ml) was emulsified with an aqueous solution of the required alkali carbonate. The advantage of this method is that molecules of the alkali soap form gradually in the droplet surfaces during the emulsification process and distribute themselves in a thin layer on the interphase boundary without aggregating. The carbonate solution is added until an emulsion of high - or maximum - concentration is formed. As in the formation of direct emulsions of maximum concentration, the end of emulsification is readily established by the appearance of the first small amount of aqueous solution of the salt which fails to disperse. If the disperse phase of the emulsion is to be an aqueous solution of another salt (not a carbonate), a benzene solution of oleic acid is first treated with a solution of carbonate of a concentration sufficient to form the soap. An aqueous solution of the required salt is then emulsified by small additions.

As previously, a complete microscopical analysis of the degree of dispersion of the emulsions was carried out, and the results were used for plotting differential curves of droplet size distribution, and the protective adsorptional-solvation layers at the droplet surfaces were also investigated [4].

Characteristics of the Emulsions

Emulsions of the w/o type were obtained over a wide range of stabilizer concentration. The tables give the following values: the maximum volume V_{∞} of the emulsified aqueous solution of the salt in 1 ml benzene, the surface S_{∞} of the adsorptional-solvation layers formed from 1 ml of the dispersion medium in the limiting emulsion, the minimum layer thickness δ_{crit} , the surface \underline{S}_0 per molecule of the stabilizer in the adsorptional layers, and the mean droplet diameter \bar{d} .

Table 1 gives the characteristics of w/o type emulsions stabilized with the "classic" emulsifier for direct emulsions - sodium oleate. The disperse phase was an aqueous solution of NaCl with a concentration of 2 moles/liter, and the disperse phase was benzene.

Emulsions of maximum concentration of the w/o type are also obtained with other alkali oleates. Table 2 gives details of such emulsions with ammonium oleate, in which the dispersion medium was again benzene, and the disperse phase was an aqueous solution of ammonium carbonate with a concentration of 2 moles/liter.

Analysis of Tables 1 and 2 shows that the laws established by us previously for direct highly concentrated

TABLE 1
Emulsions of Maximum Concentration, of the w/o Type with Sodium Oleate.

Concentration of sodium oleate in moles/liter	V_{∞} in ml	δ_{crit} in μ	S_{∞} in m^2	S_0 in A^2	\bar{d} in μ
0.14	56	0.026	38	45	1.6
0.33	96	0.011	91	45	1.7
0.48	112	0.008	125	43	1.6
0.55	116	0.007	143	43	1.3
0.64	120	0.006	167	43	1.4
0.76	125	0.006	167	36	1.3
0.82	130	0.006	167	34	1.2

TABLE 2
Emulsions of Maximum Concentration of the w/o Type with Ammonium Oleate

Concentration of ammonium oleate in mole/liter	V_{∞} in ml	δ_{crit} in μ	S_{∞} in m^2	S_0 in A^2	\bar{d} in μ
0.06	32	0.020	50	138	1.3
0.14	72	0.012	83	98	1.3
0.35	117	0.005	200	95	1.2
0.50	126	0.004	250	83	1.2
0.67	128	0.003	333	82	1.1
0.84	131	0.003	333	66	1.1
1.00	145	0.003	333	55	1.1

emulsions [4, 5] are valid for reverse emulsions. It is particularly interesting that as the soap concentration increases, the maximum thickness δ_{crit} of the nonaqueous adsorptional-solvation layers decreases, and in the high concentration region δ_{crit} reaches a constant value characteristic for each individual stabilizer. The value of the protective layer area S_{∞} varies in the opposite direction, and this also attains a constant value in the same range of high stabilizer concentrations.

From the values of S_0 (the surface area per one molecule of soap) another important conclusion follows, namely: the adsorptional layers in reverse emulsions are monomolecular and attenuated, as in direct emulsions. This conclusion is particularly important, as in the formation of w/o type emulsions in the conditions used, the nature of the stabilizer — alkali oleate — does not change, as it would in its conversion into a bivalent soap. Regardless of whether w/o or o/w emulsion is

formed, stabilization is always effected by adsorptional monolayers of soap with constant structure, the molecules of which arrange themselves in the interphase surface in accordance with the theory of diphilic molecules. It is seen that if the nature and structure of the adsorptional layers of the stabilizer are constant, the type of emulsion in our experiments is determined by the properties of the polar liquid in contact with the oil phase.

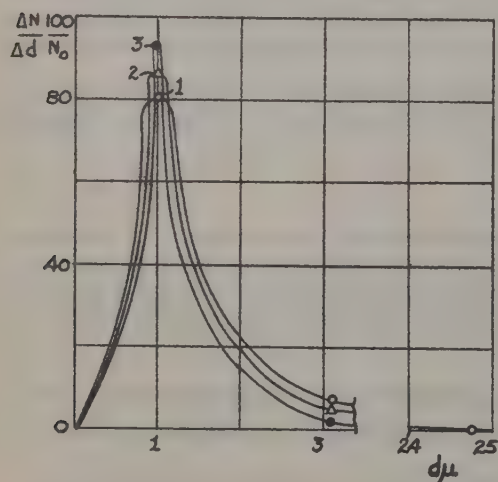


Fig. 1. Size distribution curves of droplets in w/o type emulsions with sodium oleate; concentration: 1) 0.14; 2) 0.55; 3) 0.82 mole/liter.

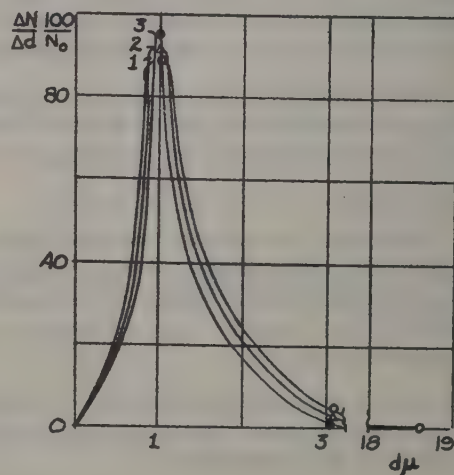


Fig. 2. Size distribution curves for droplets in w/o type emulsions with ammonium oleate; concentrations: 1) 0.06; 2) 0.50; 3) 1.0 mole/liter

The degree of dispersion of reverse emulsions is very high, and is illustrated by the values of the mean droplet diameter \bar{d} , and also by the differential size distribution curves for the droplets (Figures 1 and 2). In complete agreement with our analysis of the size decrease, increase and stabilization of droplets [7], the maximum on the distribution curves, not only for direct but also for all reverse emulsions, corresponds to the critical droplet size $2r = 1\mu$.

To obtain reverse emulsions of maximum concentration with constant values of δ_{crit} and S_{∞} it is not necessary to use very concentrated solutions of electrolyte. A constant value of δ_{crit} and S_{∞} is reached at a certain elevated concentration of salt. As an example, Table 3 shows the characteristics of reverse emulsions with aqueous solutions of NaCl of various concentrations.

TABLE 3
Characteristics of Emulsions of Maximum Concentration of the w/o Type for Various Concentrations of NaCl in the Water; Sodium Oleate Concentration 0.64 mole/liter.

Concentration of NaCl, in mole/liter	V_{∞} , in ml	δ_{crit} , in μ	S_{∞} , in m^2	S_0 , in A^2	\bar{d} , in μ
0.3	57	0.011	91	23	1.3
0.6	60	0.009	111	30	1.3
1.0	74	0.007	143	37	1.2
1.8	125	0.006	167	43	1.3
2.8	125	0.006	167	43	1.3
3.5	120	0.006	167	43	1.2

TABLE 5
Emulsions of Maximum Concentration of the w/o Type with Aqueous Solutions of Certain Salts; Ammonium Oleate Concentration 0.67 mole/liter

Electrolyte	Concentration of electrolyte in mole/liter	δ_{crit} , in μ	S_{∞} , in m^2	S_0 , in A^2	\bar{d} , in μ
$(NH_4)_2SO_4$	2.0	0.005	200	50	1.3
NH_4Cl	2.0	0.005	200	50	1.3
NH_4NO_3	2.0	0.005	200	50	1.6
NH_4CNS	2.0	0.004	250	62	1.4

emulsions of maximum concentration by ammonium oleate at different electrolyte concentrations in the water give analogous results (Table 4).

Reverse emulsions of maximum concentration are also obtained with aqueous solutions of other salts, as is seen from Table 5.

It must be stressed that these emulsions of the w/o type were also of a very high degree of dispersion, and contained over 95% droplets of the critical diameter $2r \approx 1\mu$. Thus, reverse emulsions of maximum concentration may, with every good reason, be considered as practically monodisperse systems.

Stability of Reverse Emulsions of Maximum Concentration

Reverse emulsions of maximum concentration have the same high aggregative stability as direct emulsions. As an example, Table 6 shows data on the separation of

TABLE 4
Characteristics of Reverse Emulsions of Maximum Concentration for Various Concentrations of Ammonium Carbonate in Water; Ammonium Oleate Concentration 0.67 mole/liter.

Salt concentration, in mole/l.	V_{∞} , in ml	δ_{crit} , in μ	S_{∞} , in m^2	S_0 , in A^2	\bar{d} , in μ
0.3	85	0.007	143	35	1.5
0.6	102	0.005	200	50	1.2
1.0	109	0.004	250	62	1.2
1.5	128	0.003	333	82	1.1
2.0	132	0.003	333	82	1.1
2.6	128	0.003	333	82	1.1

At a concentration of NaCl ~ 1.8 mole/liter δ_{crit} and S_{∞} first reach constant values, which do not change with further increase of the salt content in the water. Reverse emulsions are also obtained below this concentration, but their stabilization is effected by thicker adsorptional layers. Finally, at NaCl concentrations less than 0.3 mole/l, stabilization of reverse highly concentrated emulsions ceases, but direct emulsions of limiting concentration then arise in these conditions [2]. Other alkali cations act similarly.

Experiments on the stabilization of reverse

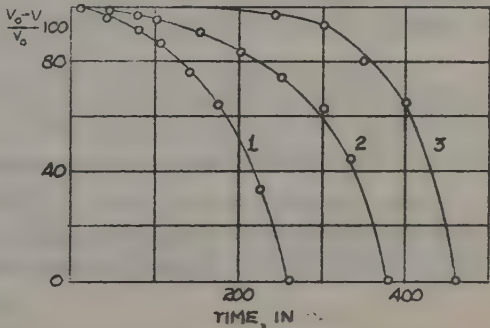


Fig. 3. Destruction of reverse emulsions of maximum concentration: 1) Ammonium oleate; 2) sodium oleate; 3) triethanolamine oleate.

the disperse (aqueous) phase and breaking of the emulsions, and also on changes of δ_{crit} and S_{∞} during aging in graduated cylinders at room temperature. The destruction of the emulsions is characterized by values of $\frac{V_0 - V_{\tau}}{V_0} \cdot 100$, where V_0 is the original volume of the emulsion and V_{τ} its volume at the aging time τ .

TABLE 6

Aging of Reverse Emulsions of Maximum Concentration; Sodium Oleate Concentration 0.67 mole/l; Disperse Phase — Aqueous Solution of NaCl.

Aging time τ , in days	$\frac{V_0 - V_{\tau}}{V_0} \cdot 100$	δ_{crit} , in μ	S_{∞} , in m^2
0	100	0.006	167
1	100	0.006	167
10	100	0.006	167
40	100	0.006	167
60	98.4	0.006	167
80	96.6	0.007	143
130	95.3	0.009	111
150	90	0.011	91
200	83.1	0.017	59
250	73.8	—	—
300	63.1	—	—
330	44.6	—	—
380	Complete destruction		

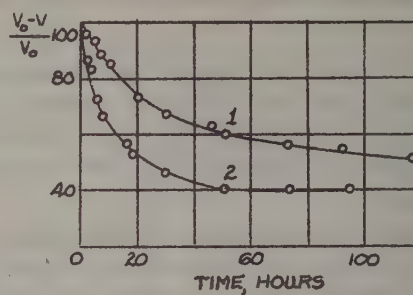


Fig. 4. Isotherms of demixing of dilute emulsions: 1) ammonium oleate; 2) sodium oleate.

The nature of the destruction of emulsions with ammonium oleate, and also of the reverse emulsions of maximum concentration with triethanolamine oleate studied by us previously [6], is the same as in the case of sodium oleate, as can be seen from Figure 3.

The period of complete stability of the emulsions (absence of separation of aqueous phase, constant values of δ_{crit} and S_{∞}) is determined by the properties of the stabilizer. Thus, emulsions with triethanolamine oleate begin to break slightly only after 240 days. The destruction increases with age, and is completed after 460 days. In the case of emulsions with sodium oleate, the separation of aqueous solution begins considerably earlier, after 60 days, and is concluded at the end of time $\tau = 380$ days. Emulsions with ammonium oleate are even less stable; their destruction begins on the 11th day of aging, and complete breaking of the emulsions occurs after 260 days.

Until destruction begins, the degree of dispersion of the emulsions remains practically unchanged, as can be seen from the values of δ_{crit} and S_{∞} in Table 6. Only after the start of destruction do the protective layers thicken and the interphase surface S_{∞} decrease. This is the result of an increase in droplet size, both by coalescence and by a process similar to the isothermal distillation of small droplets of a mist into the surface of large drops [7].

Dilution of Limiting Emulsions of Maximum Concentration

It is clear from the above that reverse highly concentrated emulsions have fairly good aggregative stability. The aggregative and kinetic stability of less concentrated emulsions, obtained by dilution of limiting systems with nonaqueous liquids, is also of interest. We must point out that we first showed a long time ago that direct emulsions of maximum concentration are readily diluted by the dispersion medium with formation of stable, less concentrated emulsions [3], which is of undoubted practical importance.

The reverse emulsions were diluted in cylinders by gradual addition of gasoline and shaking. The degree of dispersion of the diluted emulsions does not vary, and is practically the same as that of the original systems. Therefore the structure of the adsorptional layers in the diluted emulsions does not differ from the structure of the adsorptional layers in the original highly concentrated systems.

Figure 4 shows isotherms of demixing of diluted reverse emulsions with a phase volume ratio of 1:1. It is seen that demixing proceeds rapidly at first, then slows down, and ceases when a layer of "cream" with 70-71% of the disperse phase is formed. Light stirring restores the system to its original state.

CONCLUSION

The present investigation, together with our previous papers [4,5,6] conclusively proved the possibility of stabilization both of direct and of reverse emulsions of any concentration, up to the limit, with the aid of the same stabilizer. Information concerning the hydrophilic or oleophilic character of the stabilizer with respect to the pure liquids of the emulsion is not sufficient in emulsification. Variation of the properties of one of the liquids, water,

by dissolving salts in it which do not react chemically with the stabilizer, leads to salting out of the soap into the interphase surface, since it is insoluble in benzene. The polar groups of the salted-out soap are only weakly hydrated by the aqueous phase, and solvation of the hydrocarbon chains begins to prevail, although the hydrophilic character of the alkali soap toward pure water does not disappear.

The action of salts may be seen from experiments with aqueous solutions of sodium oleate in contact with benzene. As soon as the soap solution is brought in contact with a mixture of NaCl and benzene, a continuous white layer of salted-out oleate is formed in the interphase boundary. It is interesting that the degree of salting out does not depend on the original concentration of soap in the solution at a constant electrolyte content (Table 7).

TABLE 7
Salting out of Sodium Oleate; Concentration of NaCl
0.5 mole/liter.

Original concentration of sodium oleate in mole/l	Amount of soap salted out, in %	Original concentration of sodium oleate in mole/l	Amount of soap salted out, in %
0.04	72.5	0.18	71.7
0.08	71.3	0.23	71.3
0.12	72.5	0.30	71.7

TABLE 8
Salting out of Sodium Oleate from Aqueous Solutions with a
Concentration of 0.08-0.3 mole/liter.

Concentration of NaCl in mole/liter	Soap salted out, %	Concentration of NaCl in mole/liter	Soap salted out, %
0.125	33.8	0.4	66.3
0.25	49.5	0.5	71.3
0.3	57.5	1.0	91.2

One of the main results of our study is that not only direct, but also reverse emulsions are stabilized by the same adsorptional monolayers, including considerably attenuated ones. It appears from the values of S_{∞} that the emulsifying power of alkali oleates in the formation of reverse emulsions is considerable. At the same time the emulsions are fairly stable, are not destroyed for a long time, and do not change in their dispersivity during aging. In diluted emulsions the droplets also do not coalesce for a long time. Thus, the frequently met view that w/o type emulsions have low stability is without foundation. At the same time it must be stressed that even in dilute emulsions the droplets are stabilized by the same adsorptional monolayers as are found in limiting emulsions.

SUMMARY

1. Reverse emulsions of maximum concentrations have been prepared with the aid of typical hydrophilic stabilizers - alkali oleates - in presence of univalent cations. The stabilization of such emulsions commences in conditions of considerable salting out of the soap into the interphase surface.

2. Reverse emulsions of maximum and lower concentrations are stabilized by the same adsorptional monolayers, including considerably attenuated ones, as direct emulsions.

3. The degree of dispersion of the reverse emulsions is very high. The maximum on the size distribution curves always corresponds to droplets of the critical size of the order of 1μ .

4. Reverse emulsions of maximum concentration are fairly stable and remain at a constant degree of dispersion for a considerable time. Less concentrated emulsions, obtained by dilution of limiting systems, also have adequate stability.

It is our pleasant duty to express our sincere gratitude to Academician P. A. Rebinder for his constant interest in our investigations in the emulsion field, and for frequent valuable comments in discussions of our papers.

But the salting-out effect is caused by the salt concentration, as is confirmed by the data in Table 8.

Comparison of the data of Tables 3 and 8 shows that reverse highly concentrated emulsions are first formed at a NaCl concentration of 0.3 mole/l, when more than 50% soap is salted out of the aqueous solution. At lower concentrations of salt in the soap solutions, as was found previously [2], direct emulsions are still stabilized. A constant value of δ_{crit} and S_{∞} corresponds to NaCl concentrations (over 1 mole/l) which completely salt out sodium oleate.

Experiments on stabilization of reverse emulsions with triethanolamine oleate [6] were also carried out by salting out the stabilizer by means of salts out of aqueous solutions, but in this case the oleate could dissolve in benzene. Other oleates are insoluble in benzene and spread on the surface during salting-out.

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DEPENDENCE OF THE SOLUBILIZATION OF CERTAIN ORGANIC LIQUIDS ON THE CONCENTRATION OF THE SOLUBILIZING AGENT

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Colloidal dissolution (or solubilization) consists of the spontaneous passage into solution of insoluble or sparingly soluble substances by the action of surface-active additions to the solvent; it is observed and utilized in a number of diverse natural phenomena and technological processes — in the assimilation of fats by the organism, in the washing action of soaps [1], for intensification of the bactericidal action of phenols and cresols [2], in the introduction of medical products of a lipid nature into aqueous media of living organisms, for example, anticarcinogenic polycyclic preparations [2], in emulsoid sol technology [3], lubricant technology [4], in the production of margarine, etc.

In addition, it has been now established for the first time by the work of Yurzhenko [5] that emulsion polymerization of hydrocarbons, which is of great industrial importance for the production of synthetic polymers (rubbers and plastics) passes to a considerable extent through a stage of solubilization of the monomers in the emulsifier micelles. However, despite the great practical value of this effect, its mechanism is not sufficiently understood.

Elucidation of the mechanism of solubilization is made more difficult by the fact that at the present time there is no final solution to the problem of the structure of solutions of semicolloids — soaps, which, according to modern views, are characterized by a multiplicity of micelle forms coexisting in dynamic equilibrium.

On the basis of x-ray investigations it may be considered that the most probable mechanism of solubilization of hydrocarbons in aqueous solutions of soaps is their penetration into the inner hydrophobic portion of the micelles, while molecules of polar substances are included between the soap molecules in solubilization, and place themselves almost parallel to the latter, giving mixed micelles [2].

Despite the abundant experimental material, the literature does not contain any generalized view concerning the dependence of solubilization on the concentration of the surface-active semicolloid ("soap"), which is apparently to be explained by the specificity of behavior of various semicolloidal electrolytes with change of concentration [6]. For example, we were able to show [7] that in dilute solutions the direct intramicellar solubility (for benzene in aqueous solutions of Aerosols*) and the reverse solubility (for water in aqueous solutions of Aerosols), calculated in gram-molecules of the dissolved substance per 1 mole of the surface-active semicolloid, are almost independent of the concentration of the latter; that is, the concentration of the dissolved substance increases linearly with the concentration of the substance which assists solubilization.

A similar linear dependence is indicated by Yurzhenko [5], who studied the mechanism of formation of synthetic latexes in relation to the process of solubilization of monomers in aqueous solutions of emulsifiers, and also McBain and co-workers [8] for the solubilization of certain hydrocarbons in aqueous solutions of potassium and sodium oleates. Other workers, on the contrary [9] consider that the dependence of the amount of dissolved hydrocarbon on the emulsifier concentration is not linear (for sodium laurate and other sodium salts of saturated fatty acids). There are also indications that for certain synthetic soap-like substances the curve for the dependence of the intramicellar solubility on concentration passes through a maximum [6].

It might be supposed that the dependence of solubilization on concentration is chiefly determined by changes in the nature of the micellar structures with increase of the semicolloid concentration. However, the concentration range of the solubilizing substance studied by various authors was very small. We, therefore, made a detailed study of the solubilization of certain hydrocarbons and polar liquids in aqueous solutions of surface-active substances over a wide range of concentrations of the latter

The Substances Studied and Methods of Measurement

Substances studied. As surface-active semicolloids which assist solution, we used aqueous solutions or sodium

* Aerosols OT, MA, and IB, synthetic diphilic emulsifiers, are the sodium salts of the dioctyl, dihexyl, and dibutyl esters, respectively, of sulfosuccinic acid.

and potassium oleate, for two principal reasons: 1) oleates of the alkali metals are typical semicolloidal electrolytes; 2) solutions of these salts are transparent and fluid over a wide range of concentrations (up to ~30% by weight), which makes it possible to add hydrocarbons to them relatively easily and to observe the solution process with the aid of the simplest optical methods,

Solutions of sodium (and potassium) oleate were prepared by the gradual addition of the calculated amount of caustic soda to chemically pure oleic acid heated on a boiling water bath. The reaction was carried out with continuous mechanical stirring during 3-4 hours, and for more concentrated solutions, 6-8 hours.

After neutralization, the concentration of the soap solution was verified gravimetrically. The experimental error in the determination of the concentration did not exceed $\pm 0.1\%$. It was found that the pH of the sodium oleate solutions used depends only slightly on the soap concentration, and has a value of about 10* (for sodium oleate solution with a concentration of 12.5 g/100 ml, pH 9.8; 6.25 g/100 ml, pH 9.9; 1.04 g/100 ml, pH 10.1). The original solution of sodium oleate was stored in a desiccator in an atmosphere of nitrogen.

Oleic acid was prepared by hydrolysis of refined olive oil by aqueous-alcoholic alkali followed by separation from saturated acids by means of the lead salts in alcoholic solution. The oleic acid was isolated from its lead salt, distilled in a vacuum, converted into the potassium salt, and treated with barium chloride followed by extraction by a mixture of benzene and alcohol to remove any linoleic and linolenic acid present. The final purification was carried out by repeated crystallization from ethyl alcohol and vacuum distillation. After three recrystallizations the product was a pale yellow oil, and after vacuum distillation at 232.5° (15 mm), a colorless transparent liquid. The preparation of pure oleic acid is described in detail in the literature [10]. The oleic acid used in our work for the preparation of aqueous solutions of sodium (and potassium) oleate had the following constants: d_4^{20} 0.895; m.p. 14°C ; acid value 198.2; iodine number, 90.2; n_D^{20} 1.4620. The solution of caustic soda (or caustic potash) was prepared from sticks of the hydroxide, washed in boiled, redistilled water.

In selecting the dissolved substances we chose substances which differed in polarity, which should affect their solubilization and so clarify the mechanism of that effect. For this reason the hydrocarbons chosen were octane, dodecane, benzene, and cyclohexane; and the polar derivatives, octyl alcohol, nitrobenzene, and cyclohexanol. In addition, acrylonitrile and its less polar analog, methyl methacrylate, were investigated as they are substances used in the production of high polymers by emulsion polymerization. All the organic liquids were thoroughly purified and were used in a freshly distilled state

Methods of measurement. Several methods exist at the present time for the measurement of solubilization: the photometric or nephelometric [2, 11] method, the method based on lowering of the saturated vapor pressure [12] (for studying the solubility of volatile organic compounds), the refractometric method [12], the spectrophotometric method [2] (for colored compounds); the x-ray method [2], by changes of pH of the solution [13] (for soaps which hydrolyze in solution), etc. The use of any given method depends on the structure of the solvent and the substance being dissolved, their state of aggregation, differences of refractive index, vapor pressure of the dissolving substance, and other factors.

In the present study the chief methods used were the method of lowering the saturated vapor pressure and the refractometric method.

The method of lowering the saturated vapor pressure (as well as the refractometric method) was mainly used for the determination of solubilization of relatively volatile liquids (benzene, octane, acrylonitrile, etc.). This method is based on the fact that a solubilized substance lowers the saturated vapor pressure of the dissolving substance. A modification of the McBain apparatus [12] was used for the determinations. A simplified diagram of the apparatus is shown in Figure 1.

The experiments were carried out in an evacuated vessel. The emulsifier solution B was made free from air by repeated vacuum pumping. The hydrocarbon in part A of the apparatus was frozen. The vessel was then sealed off at the constriction and placed in a water thermostat fitted

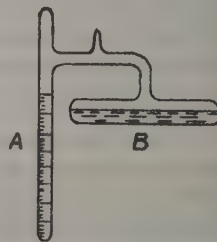


Fig. 1. Diagram of modified McBain apparatus.

* pH measurements were made with the glass electrode.

with a device for shaking. The rate of shaking was so chosen that the solution process was regular, and further increase of the shaking rate did not affect the rate of solution. A special foam-breaking device was fitted to prevent foam entering the pump during evacuation of the apparatus. The pressure during the experiments was read off with the aid of a system of manometers.

The apparatus was kept in the thermostat until equilibrium was fully established. The experiment was considered concluded when a constant pressure was established in the apparatus, corresponding to the sum of the pressures of the saturated vapors of the hydrocarbon and water, and when the meniscus of the hydrocarbon in the graduated tube *A* ceased to fall. For equilibrium to be reached in the solution of the liquids studied, 1-6 days were needed (and for solutions in gel-like systems, about one month). To obtain a more accurate value of the colloidal solubility, the amount of hydrocarbon which evaporated into the empty vessel was measured before the experiment.

Most of the measurements were made by the refractometric method proposed and developed by Yurzhenko [5]. The application of this method is based on the fact that when a hydrocarbon is added to a solution of a colloidal electrolyte, the refractive index of the solution usually increases continuously until the latter is saturated with the hydrocarbon. As partial emulsification of the hydrocarbon usually takes place during solubilization, it would be incorrect to measure the solvent power of the emulsifier solution merely by the amount of hydrocarbon introduced into the system before the refractive index becomes constant.

By Yurzhenko's method (as was later shown in detail by Peregudova and Voyutsky [14]) the solubility of liquids may be calculated on the basis of the specific refraction additivity rule. Abbe and Pulfrich type refractometers were used for refractive index determinations. With the Abbe refractometer it is possible to carry out measurements of solubility in a thin layer in highly concentrated gel-like solutions much more rapidly than in the apparatus for vapor pressure lowering.

The solubility determinations were made as follows: the hydrocarbon was added in progressively increasing amounts (up to 10-15% of the volume of the emulsifier solution) from a microburet into a series of glass ampoules, and frozen in liquid nitrogen. The hydrocarbon was measured out to an accuracy of 0.01 ml*. 20 ml of emulsifier solution of a definite concentration was then added to each ampoule; the ampoules were sealed; the mixture was shaken gently in the water thermostat until equilibrium was established, and the refractive index of the aqueous phase was then determined. The formation of an emulsion of the hydrocarbon in the emulsifier solution, as is proven, does not hinder the determination, as the microdroplets of the emulsion do not affect the refractive index but only cause light scattering.*

It should be noted that the values for solubilization obtained by different workers and with the aid of different methods, often vary considerably. To compare the results obtained by means of the methods used by us, we determined the solubilization of benzene, octane, and acrylonitrile in sodium oleate solution of a concentration of 7g/100 ml. The results are shown in Table 1.

TABLE 1
Solubility of Benzene, Octane, and Acrylonitrile in Grams per 100 ml Solution of Sodium Oleate, Determined by Various Methods at 20°

Method	Benzene	Octane	Acrylonitrile
Visual	2.60	1.00	11.20
Nephelometric	2.55	1.00	11.00
Refractometric	2.85	1.15	12.15
By lowering of saturated vapor pressure	2.57	1.05	9.50

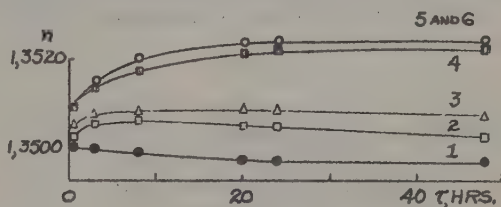


Fig. 2. Variation of refractive index in sodium oleate solution, 5g/100 ml, with time, for varying amounts of added nitrobenzene: 1) Without nitrobenzene; 2) 0.05 ml; 3) 0.1 ml; 4) 0.3 ml; 5) 0.5 ml, and 6) 0.8 ml nitrobenzene; τ is the solubilization time in hours; amount of soap solution - 30 ml.

A comparison of the results for the solubilization of nitrobenzene (determined visually from the turbidity of the solution, and refractometrically) for various concentrations of sodium oleate are shown in Table 2.

It is seen from Tables 1 and 2 that solubilization determinations by the refractive index method give higher values than those obtained by the visual method. As has been indicated, the explanation for this is, that visible turbidity as the result of emulsification appears at a somewhat lower amount of the added liquid than that at which

*Evaporation into the empty ampoule was taken into account.

TABLE 2

Solubilization of Nitrobenzene in Aqueous Solutions of Sodium Oleate at 20°

Concentration of sodium oleate		Am't of dissolved nitrobenzene in g/100 ml solution	
g/100 ml	mole, l	Criterion turbidity	Criterion refractive index
0	0	0.200	0.200
3.0	0.0980	0.720	0.720
6.0	0.197	1.44	1.68
9.0	0.290	2.26	2.65
12	0.394	4.12	5.05
15	0.493	6.51	8.42

the refractive index ceases to alter (that is, for some time the solubilization and emulsification processes take place simultaneously). The method of saturated vapor pressure lowering gives low results, apparently as the result of interdiffusion of the vapors of hydrocarbon and water even before saturation is reached (particularly in the case of liquids with a strong solvent power for water, such as acrylonitrile).

In the evaluation for the accuracy of a given method it is necessary to take into account the specificity of the substances used. For example, we found that for the determination of solubilization of organic liquids in sodium oleate solutions the refractometric method is quite suitable and gives good reproducibility of results. However, if sodium Mersolate is used as emulsifier (MK,

a mixture of sodium salts of saturated sulfonic acids), the solubility values calculated from the refractive index values of the original substances and the final solutions are higher than the total amounts of hydrocarbon taken. We determined the volume changes of the liquids on mixing and found that when organic liquids are dissolved in MK there are considerable deviations from volume additivity, and evidently this causes the error in the calculation. The deviations from additivity in the case of solubilization in sodium oleate solutions are not large, and the solubilization can be measured by the refractometric method in this case.

To obtain equilibrium values for the solubilization, it was necessary to study the kinetics of the process. Experiments, for all the concentrations of sodium oleate solutions studied, showed that twenty-four hours are sufficient for complete saturation of the solutions. As an example, Figure 2 shows the variation of the refractive index of sodium oleate solution, 5g/100 ml, with time, for various amounts of added nitrobenzene at 20°. Saturation of the solution occurs after 24 hours with additions of 0.5-0.8 ml $C_6H_5NO_2$ per 30 ml soap solution; after this n does not increase further.

The results of the experiments shown in Figure 2 may be represented in the coordinate system

$$n = f(S),$$

where S is the amount of added nitrobenzene for different solubilization times. As Figure 3 shows (similar measurements of the solution of benzene in aqueous solutions of sodium oleate were made by Peregudova and Voyutsky [14]) when the solubilization time is short, n , and therefore also the amount of dissolved nitrobenzene, depend little on the amount of nitrobenzene added to the system, apparently because solubilization does not have enough time for completion.

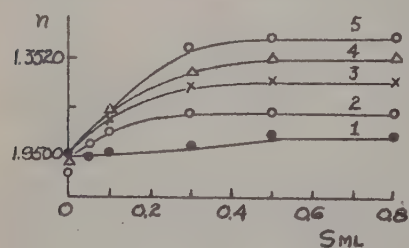


Fig. 3. Variation of the refractive index n of sodium oleate solution, 5g/100 ml, on the amount of added nitrobenzene for different times of solubilization: 1) 3 min; 2) 30 min; 3) 3 hours; 4) 8 hours; 5) 24 and 48 hours; s is ml of nitrobenzene per 30 ml of sodium oleate solution.

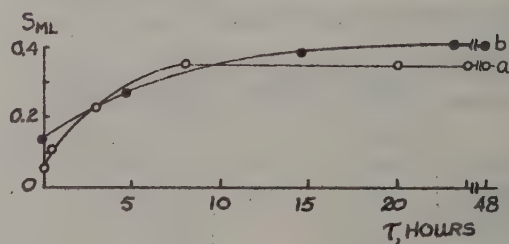


Fig. 4. Solubilization kinetics: a) Nitrobenzene in 30 ml sodium oleate solution of a concentration of 5 g/100 ml; b) octane in 20 ml sodium oleate solution of a concentration of 9g/100 ml.

Figure 4 shows the dependence of the solubility of nitrobenzene and octane in solutions of sodium oleate, calculated from the maximum values of n on the time of dissolving. The greatest solution rate is during the first 4-6 hours, and solubilization then slows down.

The solubilization of all the other organic substances studied varied with time (for different concentrations) essentially in the same way. In all subsequent experiments on refraction, the saturation of the soap solution with the solubilized liquid took 24 hours.

Results of the Determinations

The results of solubilization determinations at different concentrations of the solubilizing substance are shown in Tables 3 and 4 and Figure 5 to 7.

In view of the considerable solubility of a number of the liquids in water, and of the wide range of concentrations of the soap solutions studied,* a correction for the solubilities of these liquids in water was applied (Table 4). In Figures 5 and 6 the dotted lines indicate the solubility of acrylonitrile and methyl methacrylate in the aqueous phase of the solution.

TABLE 3
Solubilization of Hydrocarbons in Aqueous Solutions of Sodium Oleate at 20°

Hydrocarbons	Concentration of sodium oleate		Am't of hydrocarbon dissolved	
	g/100 ml	mole/liter	g/100 ml solution	mole hydrocarbon per mole soap
Octane	0	0	0	—
	5.00	0.164	0.910	0.490
	9.00	0.295	1.44	0.427
	14.0	0.460	3.08	0.586
	24.0	0.790	9.05	1.00
Dodecane	0	0	0	—
	5.00	0.164	0.32	0.115
	9.00	0.295	0.70	0.140
	14.0	0.460	1.3	0.166
	24.0	0.790	3.0	0.223
Cyclohexane	0	0	0	—
	2.00	0.0650	0.810	1.48
	5.00	0.164	1.68	1.22
	9.00	0.295	4.21	1.69
	14.0	0.460	8.00	2.06
Benzene	0	0	0.070	—
	2.00	0.0650	0.920	1.69
	5.00	0.164	2.29	1.74
	7.00	0.230	2.86	1.57
	9.00	0.295	5.63	2.42

As the results show, polar derivatives (for example, octyl alcohol and cyclohexanol) show much higher solubilization than the corresponding nonpolar liquids (for example, octane and cyclohexane). This has been noted previously by other authors [2, 15] and is apparently due to the fact that the probability of penetration of polar molecules of the solubilized liquid into the micelles through their outer hydrophilic surface (by interpenetration between the soap molecules) is greater than in the case of nonpolar molecules (the only exception is nitrobenzene which, according to our results, is rather less soluble than benzene).

Further, it is seen from Figures 5-7, which show solubilization of the organic liquids studied, in grams per 100 ml of soap solution, as a function of the soap concentration, that the increase of

the solubility of these liquids with increasing soap concentration follows one general law, namely: up to soap concentrations of 7-9 g/100 ml the solubilization increases linearly, but at higher concentrations its increase is more rapid [7].

The lack of dependence (or the very slight dependence) of solubilization on the concentration up to a definite limit, and its subsequent sharp increase is seen even more clearly from Figure 7, which illustrates the dependence of molal solubility of organic liquids on the concentration of aqueous sodium oleate solution (the molal solubility in the region up to 9 g/100 ml = 0.23-0.295 mole/l sodium oleate is constant, and the straight line in this region of concentrations is parallel to the abscissa axis).

The solubilization values, especially in concentrated solutions of soap, are fairly high. For example:

* The solubilization of some of the liquids (octyl alcohol, benzene) was studied only for soap concentrations up to 9-15 g/100 ml. The reason for this was that when these liquids were added to soap solutions of higher concentration, either emulsification or considerable thickening of the system took place, which hindered determination of solubilization.

TABLE 4

Solubilization of Polar Organic Liquids in Aqueous Solutions of Sodium Oleate at 20°

Organic liquids	Concentration of sodium oleate		Amount of organic liquid dissolved			
	g/100 ml	mole/l	g/100 ml solution			mole organic liquid per mole soap
			Total in solution	In water	In sodium oleate	
Octyl alcohol	0	0	0.100	0.10	—	—
	5.0	0.164	5.50	0.095	5.41	2.52
	9.0	0.295	14.2	0.091	14.1	3.65
Cyclohexanol	0	0	6.200	6.2	—	—
	5.0	0.164	18.54	5.9	12.64	7.70
	9.0	0.295	37.92	5.6	32.32	10.9
	14.0	0.460	123.6	5.3	118.3	25.6
Nitrobenzene	0	0	0.20	0.20	—	—
	3.00	0.0980	0.72	0.20	0.52	0.43
	6.0	0.197	1.68	0.19	1.49	0.61
	9.0	0.290	2.65	0.18	2.47	0.69
	12.0	0.394	5.05	0.17	4.88	1.0
	15.0	0.493	8.42	0.17	8.25	1.4
Acrylonitrile	0	0	8.50	8.5	—	—
	3.0	0.098	9.72	8.3	1.42	2.73
	6.0	0.197	12.2	8.1	4.05	3.88
	9.0	0.290	12.2	7.8	4.35	2.82
	12.0	0.394	14.6	7.6	6.93	3.30
	15.0	0.493	21.1	7.5	13.6	5.17
	26.2	0.868	48.6	6.6	42.0	9.10
	35.7	1.17	97.2	5.9	91.3	14.7
Methyl methacrylate	0	0	0.800	0.80	—	—
	3.0	0.098	1.52	0.80	0.72	0.73
	6.0	0.187	2.85	0.75	2.10	1.06
	9.0	0.290	4.28	0.73	3.55	1.23
	12.0	0.394	5.69	0.70	5.00	1.27
	15.0	0.493	7.60	0.68	6.92	1.40
	26.2	0.868	18.9	0.60	18.4	2.14

9 g/100 ml sodium oleate dissolved 4 moles/l. octyl alcohol }
 14 " " " " 9 " acrylonitrile } per mole per liter of soap, respectively.
 26 " " " " 25 " cyclohexanol }

From this variation of the solubilization with concentration, which shows that soap, particularly in concentrated solutions, retains a disproportionately large amount of organic liquids, we may conclude that this is due to changes, with variation of concentration, of the micellar structures in soap solutions.

Indeed, the lack of dependence (or the small increase) of solubilization on concentration for most liquids (all the hydrocarbons and some of the polar liquids) is evidently due to the fact that in this region, which is above the critical concentration of micelle formation (CCM for sodium oleate is 0.03-0.04% [2, 16]), the nature of the micelles apparently does not vary with increase of concentration.

The subsequent sharp increase of the solubilities of all the liquids at concentrations above 9g/100 ml may be attributed to a deeper modification of the micellar structures in the solution of the surface-active semicolloid, for example, by the conversion of a majority of the spherical micelles into micelles of laminar form, by the appearance of continuous micellar layers, a continuous structural network, etc.

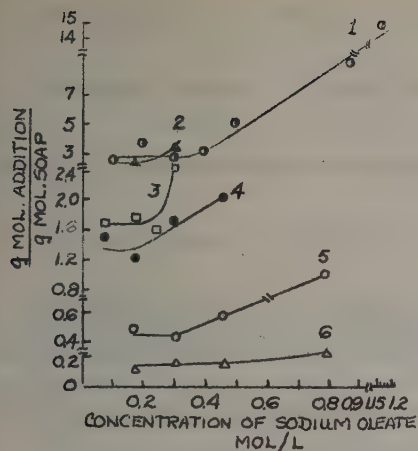


Fig. 5. Dependence of the molal solubility of organic liquids on the concentration of aqueous sodium oleate solution: 1) Acrylonitrile; 2) octyl alcohol; 3) benzene; 4) cyclohexane; 5) octane; 6) dodecane.

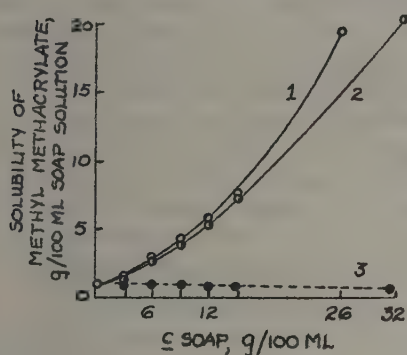


Fig. 7. Solubilization of methyl methacrylate in aqueous solutions of: 1) Sodium oleate; 2) potassium oleate; 3) in pure aqueous medium.

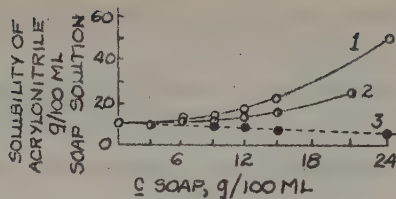


Fig. 6. Solubilization of acrylonitrile in aqueous solutions of: 1) Sodium oleate; 2) potassium oleate; 3) in pure aqueous medium.

For example, there is reason to suppose that the higher solvent power of sodium oleate solutions, in comparison with potassium oleate solutions, for acrylonitrile, and methyl methacrylate (Figures 6 and 7) is evidently also due to the fact that sodium oleate has a more highly developed structure than potassium oleate, especially at high concentrations. Therefore, 9g/100 ml sodium oleate, which is a transitional concentration with respect to its solvent power, may be termed the "critical concentration of structure formation".

Thus, the demonstrated dependence of solubilization on the concentration of the solubilizing agent indicates a definite relationship between the structure of solutions of surface-active substances and solubilization.

In this connection we carried out a detailed study of the nature of structure formation with aqueous solutions of sodium and potassium oleates in relation to the concentration of the semicolloid, and of changes in the structure of these systems during solubilization of organic liquids. The results of these investigations will be presented in a subsequent separate publication.

SUMMARY

1. Studies of the solubilization of liquid hydrocarbons (octane, dodecane, benzene, cyclohexane) and of polar liquids (octyl alcohol, cyclohexanol, nitrobenzene, methyl methacrylate, and acrylonitrile) in solutions of sodium (and potassium) oleate over a wide range of concentrations show that there is a direct relationship between solubilization and the nature of the micellar structures formed in solutions of this typical surface-active colloid.

2. The dependence of the solubilization on the soap concentration was studied in two concentration regions: 1) from 2 to 9g/100 ml, and 2) from 9 to 24g/100 ml. In the first region the solubilization of most of the liquids is practically independent of the concentration. It may be assumed that the structure of these colloidal solutions also does not change with concentration.

3. At a sodium oleate concentration of 9g/100 ml there is a transition in the solvent power of the sodium oleate solution, and from that point increase of concentration is accompanied by a sharp increase of the solvent power of the soap, which is apparently due to changes in the character of structure formation in the soap solution.

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EXPERIMENTAL INVESTIGATIONS OF LAMINAR SYSTEMS

XXI. EFFECT OF ELECTROLYTES ON THE FORMATION OF ULTRA-THIN FILMS ON THE SURFACE OF COLLOIDAL SOLUTIONS OF TITANIUM AND THORIUM HYDROXIDES

S. G. Mokrushin and Z. G. Sheina

The aim of the work was to elucidate the possibility of spontaneous formation of ultra-thin films on the surface of hydrosols of positively charged titanium and thorium hydroxides, and also to study the effect of electrolytes on the formation time of the films. The method of investigation used in this work was described previously [1]. The titanium and thorium hydroxide sols were prepared by hydrolysis, by adding solutions of titanium (or thorium) tetrachloride drop by drop to boiling distilled water, followed by dilution with cold water.

Titanium hydroxide hydrosol was prepared by the addition (drop by drop) of 1.5-2 ml titanium tetrachloride solution (3%) to 0.5 l boiling water; when a visible opalescence appeared, this solution was poured into 1.5 l cold distilled water. The sol obtained was diluted 8 times, and the diluted solutions poured into open vessels for the formation of films of colloidal titanium hydroxide on the surface of the sols.

Titanium hydroxide sol obtained by the above method has a positive charge, and therefore formation of surface films can be expected in accordance with earlier results for iron and aluminum hydroxides [1]. In fact, experiments confirmed this supposition. On the assumption that the formation of the surface film is the result of surface coagulation of the hydroxide micelles by anions present in excess in the surface layer, experiments were performed to find the effect of electrolytes: potassium chloride, bromide, and iodide, on the formation time of the film. According to Frumkin [2], the anions of these salts pass preferentially into the surface layer and set up a negative charge in the surface of the liquid. Preliminary experiments showed that 25 ml of 0.1 N solution of electrolyte in 2.5 l of the sol do not cause visible coagulation with the formation of a precipitate. The thickness of the spontaneously formed films on the sol surface was determined by the Langmuir-Blodgett method, the refractive index of titanium hydroxide films having been first determined with the aid of Brewster's law. The mean value of the refractive index was 1.42. The multilayer films, obtained on polished chrome-plated surfaces, were of a blue color. The results of the experiments on the effect of electrolytes on film formation are shown in Figure 1.

As the experimental results show, the effect of anions — chloride, bromide, and iodide — depends on the power of the ions to become concentrated in the surface layer, in agreement with Frumkin's investigations [2], so that iodide anions have the greatest effect in the first period of film formation (less than twenty-four hours).

However, after that time, bromide anions had a stronger effect on the film formation process. It is possible that this discrepancy may be explained by surface oxidation of the iodide anions, as during the experiments evolution of iodine was observed on the cardboard cover of the vessel with the sol, and an odor of iodine was noticed. As the result of oxidation, the concentration of anions in the surface layer decreased, and the effect of the iodide anions became less. At the same time it is necessary to note that latent coagulation of the micelles apparently took place in the volume of the sol, as the maximum thickness of the film was greater for sols with potassium bromide additions. To study the effect of electrolyte concentration on the kinetics of formation of titanium hydroxide films, experiments were carried out in which 25 ml of potassium chloride solutions, with concentrations of 0.1, 0.05, and 0.01 mole/l. were added to 2.5 l of the sol. The effect of potassium chloride concentration on the time of film formation is shown in Figure 2. As can be seen from Figure 2, film formation is accelerated with increase of electrolyte concentration, but the maximum film thickness (after 16 days) is the same in all cases, and is equal to 43.1 Å.

The addition of a nonpolar liquid (benzene) to the surface of the sol should favor the retention of the colloidal particles of titanium hydroxide on the sol surface and so assist film formation. This effect of nonpolar liquids on hydrophobic colloidal particles follows from the principle of difference of polarities which was put forward by Rebinder [3], and also from the general thermodynamic principle that a system tends to have minimum free energy, which in this case is the free surface energy of the colloidal particles in the surface film [4]. These

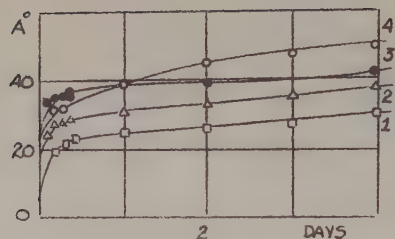


Fig. 1. Effect of electrolytes on the formation of Ti(OH)_4 film: 1) Without added electrolyte; 2) KCl; 3) KI; 4) KBr.

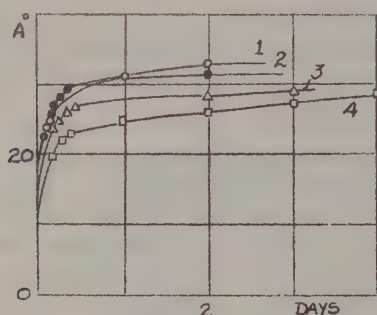


Fig. 2. Effect of concentration of KCl solution on the formation of Ti(OH)_4 film: 1) 0.1; 2) 0.05; 3) 0.01 mole/l; 4) without added electrolyte.

corresponded to the values of the negative potential of the sol surface, in agreement with the work of Frumkin [2]. Thus, with trichloroacetic acid the maximum thickness was reached after 4 days, with dichloroacetic acid, after 12 days, and with monochloroacetic, after 14 days. The effect of additions of benzoic acid is shown in Figure 5.

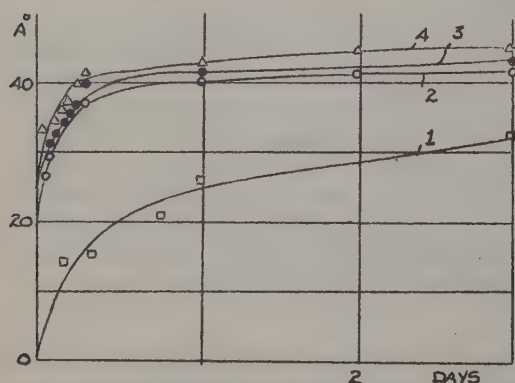


Fig. 3. Effect of electrolytes and benzene on the formation of Ti(OH)_4 films: 1) Without added electrolyte; 2) KCl; 3) KI; 4) KBr.

views were confirmed experimentally; the experiments were carried out as follows: 2.5 l of the sol was placed in the bath, and 2.5 ml of electrolyte of the appropriate concentration was then added. After the sol was mixed with the electrolyte, a layer of benzene was poured on the surface of the sol, and this was allowed to evaporate gradually (in the course of an hour) from the sol's surface. During this time an invisible film of colloidal hydroxide particles formed on the surface of the sol. A multilayer film, blue in color, was obtained by repeated immersion of a chrome-plated plate in the sol. The results of the experiments are shown in Figure 3 which shows that bromide ions had the greatest effect.

The effect of the electrolytes: potassium chloride, bromide, and iodide, and ammonium thiocyanate, on the time of film formation is manifested in the initial stages, during the first 6 hours, before the film reaches its maximum thickness. For all electrolyte additions the maximum thickness has the same value - from 36 to 37 A. In their effect on the time of film formation the ions fall in the following series:



The effect of increasing additions of ammonium thiocyanate is shown in Figure 4, from which it is seen that addition of thiocyanate ions produces coagulation within the volume of the sol, as the maximum film thickness is far greater than for the original sol. The time required for the formation of the film of maximum thickness depends on the amount of ammonium thiocyanate added. For example, a film thickness of 57 A was attained in 6 hours by the addition of 25 ml of 0.1 N ammonium thiocyanate solution, and only after 8 days by the addition of 10 ml of the same solution. The effect of additions of chloroacetic acids (mono, di, and trichloroacetic) on the time of formation of films of maximum thickness

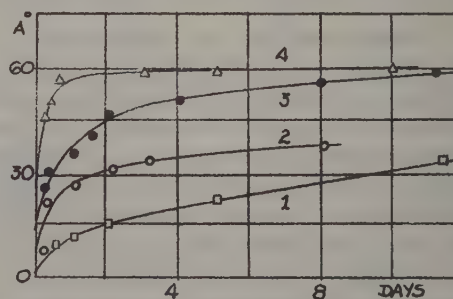
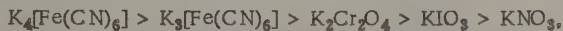


Fig. 4. Effect of NH_4CNS concentration on the formation of Ti(OH)_4 films: 1) Without added electrolyte; 2) 1 ml; 3) 10 ml; 4) 25 ml; of 0.1 M solution of NH_4CNS per 2.5 liters of sol.

A study of the effect of the electrolytes $\text{K}_4[\text{Fe(CN)}_6]$, $\text{K}_3[\text{Fe(CN)}_6]$, $\text{K}_2\text{Cr}_2\text{O}_7$, KIO_3 , KNO_3 on the formation of a surface film of colloidal titanium hydroxide showed that addition of 0.01 M

electrolyte solution in the amount of 20 ml per 2 l of the sol produces volume coagulation. Coagulation with the formation of a precipitate took place immediately on the addition of $K_4[Fe(CN)_6]$ solution and after one hour in the case of $K_3[Fe(CN)_6]$, and therefore the formation of colloidal film was not studied with these electrolytes. Addition of the electrolytes K_2CrO_4 , KIO_3 , and KNO_3 gave the following thicknesses of colloidal titanium hydroxide films formed after twenty-four hours on the undisturbed sols: 47.0, 35.7, and 28.7 Å respectively. These results are in agreement with the electrolyte series



found by Weiser [5] for the coagulation of positively charged titanium hydroxide sol.

To determine the effect of dilution of the sol on the maximum film thickness, experiments were carried out with titanium hydroxide sol (concentration 0.013% TiO_2) diluted 2, 4, 6, and 8 times. The experiments showed that the maximum film thickness is independent of dilution, and is 31 Å

The process of film formation and the attainment of maximum thickness was also studied with the aid of the Marselen apparatus [6]. The compression of the film was measured from the angle of twist of the wire of the apparatus. The compression was expressed in the form $(S_0 - S)/S_0$, where S_0 is the area of the film before compression, S is the area of the film under a compression corresponding to the angle of twist α of the wire of the Marselen apparatus.

The results of the determinations are shown in Figure 6.

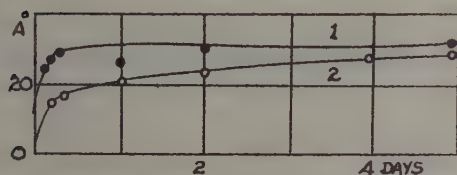


Fig. 5. Effect of benzoic acid on the formation of $Ti(OH)_4$ films; 1) C_6H_5COOH ; 2) without addition.

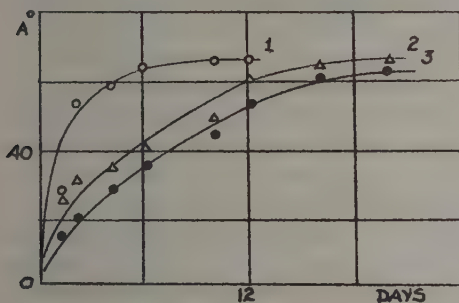


Fig. 7. Effect of dilution on the formation of $Th(OH)_4$ film; 1) Original sol; 2) diluted 2 times; 3) 4 times.

ments indicate that the thickness of the compressed film is constant, or, in other words, that the film is of monomolecular thickness. At the same time, the film compression experiments once again confirm the concept of film formation as surface coagulation of colloidal particles (micelles), first with formation of "islands", the thickness of the original primary colloidal particles. The "islands" formed join together to form a net-like structure, which is then transformed into a more dense surface film.

In conclusion, experiments were carried out with positively charged colloidal particles of thorium hydroxide.

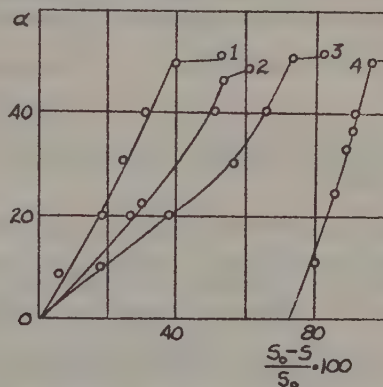


Fig. 6. Dependence of the compression of $Ti(OH)_4$ films on their formation time: 1) 24 hours; 2) 4 hours; 3) 1 hour; 4) less than an hour.

It is seen from Figure 6 that the film formed in the first instant after the sol is poured into the bath apparently consists of very minute aggregates or "islands" of colloidal particles floating on the surface of the sol, as a result of which the film can be compressed to 94% of the original surface at a pressure corresponding to a twist angle of 50° . After an hour of the film formation process, the film can be compressed only to 72% for $\alpha = 50^\circ$. With further compression to 81° the twist angle remains constant, indicating destruction (breakage) of the film. The same is found 4 hours and twenty-four hours after the start of film formation, that is, the twist angle remains constant ($45-50^\circ$) on further compression of the film. These experi-

The thorium hydroxide sol was prepared by hydrolysis. The concentration of the sol obtained was 0.044 % (from the ThO_2 content). The refractive index of the thorium hydroxide films, determined by Brewster's law, was 1.26.

Experiments were carried out with this sol to show the dependence of the film thickness on the concentration. The results are shown in Figure 7.

As is seen from Figure 7, the maximum thickness of the film is almost independent of the sol concentration. The thickness of the thorium hydroxide film is greater than the thickness of titanium hydroxide film; it is very probable that thorium hydroxide sol is polydisperse, as the multilayer films obtained on a polished plate had a somewhat spotted appearance.

SUMMARY

1. It was shown experimentally that the formation of surface films on sols of titanium and thorium hydroxide is the result of coagulation of the sol particles on the separation boundary of the phases: sol - air, and sol-nonpolar liquid.

2. The effect of electrolytes (anions) on the kinetics of film formation on the surfaces of positively charged sols confirms the hypothesis of surface coagulation as a condition for the formation of monolayer films.

3. From determinations of the maximum thickness of the monolayer films it is possible, in conjunction with other methods for the determination of colloidal particle size, to obtain indications of particle shape.

A. G. Piotrkovskaya and G. G. Fedorova participated in the experimental work.

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* This reference is evidently in error, as no paper by Mokrushin and Milyutina appeared in the issue referred to.

** See Consultants Bureau Translation, page 217.

DIFFUSION OF VARIOUS SUBSTANCES THROUGH HYDRATE CELLULOSE FILMS

A. B. Pakshver and I. V. Bykova

Hydrate cellulose films (Cellophane) are used in practice as a packaging material, and therefore the interest in studies of the diffusion of various substances through these films is quite understandable. It was shown by the work of Reitlinger and other workers [1] that in established (steady) conditions, the diffusion of gases obeys Fick's law in its simplest form (in steady conditions $\frac{\partial c}{\partial t} = 0$ and $\frac{\partial c}{\partial x} = \text{const}$):

$$P = -D \frac{\partial c}{\partial x} \quad (1)$$

and hence

$$D = \frac{s P}{F (c_0 - c)} \quad (2)$$

where s is the film thickness in cm; P is the amount of substance in g/sec, which diffuses through unit area of the film in unit time; F is the area of the film in cm^2 , and c_0 and c are the concentrations of the substance in g/cm^3 on the two sides of the film.

It was found for Cellophane films that the diffusion coefficient depends strongly on the nature of the diffusing substance, and is equal to $D = 1 \cdot 10^{-10} \text{ cm}^2/\text{sec}$ for substances which do not react with cellulose, such as hydrogen. In the case of diffusion of substances which can react with cellulose, in particular, for the diffusion of water or of various substances from aqueous solution, the molecular structure of the cellulose film alters, and the coefficient of diffusion rises sharply to $5-8 \cdot 10^{-6} \text{ cm}^2/\text{sec}$ [2]. This considerable weakening of structure may be attributed to weakening of the hydrogen bonds between the cellulose macromolecules by the interaction of OH groups of hydrate cellulose with OH groups of water or bases. The process is much more complex in diffusion with an unestablished regime, when diffusion takes place into the film, the hydrate cellulose becoming saturated with the diffusing substance. This takes place, for example, in the dyeing of films or fibers with direct dyes. The rate of sorption of the dye is determined by its rate of diffusion into the mass of the hydrate cellulose, and is described by more or less complex equations obtained by resolution into series of Fick's general differential equation for diffusion [3]. In this case, the coefficient of diffusion, according to the experimental data of various authors [4], is from 2 to $5 \cdot 10^{-9} \text{ cm}^2/\text{sec}$, and depends on the concentration of added electrolyte. This great difference between the values of $\underline{D}_{\text{st}}$ and $\underline{D}'_{\text{unst}}$ may be explained on the view that in the nonsteady regime diffusion takes place in stages, moving into those regions of the fiber or film which had not yet been acted upon by water, and in which, therefore, the structure of the hydrate cellulose has not yet been weakened by the action of water. Therefore, the values of \underline{D}' approach the values of \underline{D} in the case of hydrogen and other substances which do not react with hydrate cellulose.

In diffusion through films, it is also possible to observe an initial nonsteady period when the process is not yet established, that is, the front of the aqueous solution has not yet passed through the film, and the diffusion occurs in the unweakened structure of the film. For the simplest case (the concentration of the diffusing substance within the film and on one side of the film is zero), the following equation is valid [3]:

$$L = \frac{s^2}{6 D'} \quad (3)$$

where L represents the time necessary to reach a steady state in seconds, and \underline{D}' is the coefficient of diffusion for the nonsteady state.

Experimental studies made in our laboratory showed that in the nonsteady state of the process, the coefficient of diffusion of phenol and dyes into polyamide fibers also greatly depends on the original molecular structure of the fiber [5]. Mechanical tension or heating of the fiber, and other treatments which facilitate the formation of intermolecular bonds, greatly retard diffusion. The same was found in studies of absorption of copper by hydrate cellulose fibers from cuprammonium solution. The value L is the time needed for the establishment of a constant concen-

tration difference, characterized by steady conditions, between the two sides of the film ($c_0 - c$). During the time L diffusion through the film is much slower, as the structure of the polymer film has not yet become loosened by swelling, and the coefficient D' is much less than the steady state diffusion coefficient D . The value of L may be easily found experimentally by a graphical method: for this, it is necessary to plot the amount of substance diffused through the film in unit time against time.

In this paper, we present the results of determinations of the diffusion coefficient D in steady conditions from Equation (2), and D' in nonsteady conditions from Equation (3) for hydrate cellulose and three different substances: caustic soda, which causes swelling of hydrate cellulose, glycerin, and the dye, methylene blue.

The work was carried out in a thermostat accurate to 0.1° . Ordinary hydrate cellulose (Cellophane) film, 48 to 52 μ thick, was used, from which glycerin was first removed, and the thickness of which was measured with a micrometer. To determine the diffusion rate, a glass vessel of special shape was used, one of the side walls of which was replaced by the film. The vessel was held by clamps used for osmometric determinations, and placed in the thermostat. Water was passed through this vessel in a slow stream, and the concentration of diffused material in the water leaving the diffusion cell was determined by analysis.

The experimental results shown in Tables 1, 2, and 3 were calculated from Equations (2) and (3), and also from a type of Arrhenius equation for a diffusing stream (activation energy E_D). The swelling of the films was measured directly from the film thickness with a micrometer. The relationship between the diffusion coefficient D and the molecular weight of the diffusing substance M was established by means of the equation normally applied to gaseous diffusion:

$$\frac{D_1}{D_2} = \sqrt{\frac{M_2}{M_1}} \quad (4)$$

As special experiments showed, stirring of the liquid somewhat affects the rate of diffusion. Therefore, all the experiments were carried out at a maximum rate of stirring — 1200 rev/min. It is possible to predict from general considerations [6] in which cases stirring should affect the rate of diffusion through films.

TABLE 1

Diffusion through Cellophane in Steady Conditions

Substance	Concentration (g/l)	Temperature ($^\circ\text{C}$)	Film dried at 110° under tension			Film not dried		
			% Swelling	$D \cdot 10^{-6}$	E_D	% Swelling	$D \cdot 10^{-6}$	E_D
NaOH	32.9	20	125	1.85		148	2.2	
		25		2.0	3450		2.3	2800
		30		2.25			2.55	
	16.0	20	108	1.5		123	1.65	
		25		1.65	2700		1.75	2500
		30		1.75			1.90	
	8.0	20	100	1.0		110	1.20	
		25		1.4	7200		1.45	5800
		30		1.55			1.70	
Methylene blue dye	2.72	20	84	0.195		119	0.29	
		25		0.23	6600		0.345	5000
		30		0.28			0.385	
	1.60	20	83	0.195		119	0.285	
		25		0.245	7100		0.365	5200
		30		0.295			0.380	
	0.82	20	87	0.195		119	0.295	
		25		0.24	6600		0.345	5000
		30		0.285			0.390	

(continued)

TABLE 1 (continued)

Substance	Concentration (g/l)	Temperature (°C)	Film dried at 110° under tension			Film not dried		
			% Swelling	$D \cdot 10^{-6}$	E_D	% Swelling	$D \cdot 10^{-6}$	E_D
Glycerine	61.2	20	85	0.35		117	0.51	
		25		0.43	5900		0.63	5600
		30		0.49			0.70	
	42.5	20	92	0.33		121	0.51	
		25		0.42	6200		0.63	5120
		30		0.47			0.685	
	22.6	20	89	0.34		122	0.51	
		25		0.42	6200		0.62	5200
		30		0.48			0.69	

TABLE 2

Diffusion through Cellophane in the Initial Period $s_{\text{init}} = 48 \mu$, Nonsteady Conditions, at 20°C

Substance	Concentration (g/l)	Dried film		Undried film	
		L (sec)	$D \cdot 10^{-10}$	L (sec)	$D \cdot 10^{-10}$
NaOH	32.9	4,800	8.0	3,600	10.6
Methylene blue	2.7	21,600	1.77	18,000	2.1
Glycerin	42.5	16,200	2.4	12,600	3.0

TABLE 3

Effect of Film Swelling and of Molecular Weight of the Diffusing Substance on the Value of the Diffusion Coefficient \bar{D} (Steady Conditions). Initial Conditions: Diffusion of Methylene Blue Dye ($M = 319$) at 20° and 85% Swelling
 $D_0 = 0.195 \cdot 10^{-6}$

$$k_1 = \frac{\% \text{ Swelling}}{85}$$

$$D = k_1 \sqrt{\frac{319}{M}} D_0 \quad (6)$$

Substance	Concentration (g/l)	Dried film			Undried film			% Swelling (unstretched)	% Swelling (stretched)	$D_{\text{unstretched}}$	$D_{\text{stretched}}$
		k_1	$D \cdot 10^{-6}$ (calculated)	$D \cdot 10^{-6}$ (experimental)	k_1	$D \cdot 10^{-6}$ (calculated)	$D \cdot 10^{-6}$ (experimental)				
NaOH	32.9	1.47	1.25	1.85	1.74	1.48	2.2	1.18		1.18	
	16.0	1.27	1.08	1.50	1.45	1.23	1.65	1.14		1.11	
	8.0	1.175	1.0	1.0	1.29	1.10	1.20	1.10		1.20	
Methylene blue	2.7	1.0	0.19	0.19	1.39	0.27	0.29	1.40		1.48	
	1.6	1.0	0.19	0.19	1.39	0.27	0.28	1.40		1.45	
	0.8	1.0	0.19	0.19	1.39	0.27	0.29	1.40		1.50	
Glycerin	61.2	1.0	0.36	0.35	1.38	0.50	0.51	1.39		1.45	
	45.2	1.05	0.36	0.33	1.42	0.51	0.51	1.40		1.50	
	22.6	1.05	0.36	0.34	1.43	0.51	0.51	1.40		1.50	

If a microporous solid reacts with a liquid or gas and the reaction proceeds homogeneously throughout the thickness of the solid, then, according to Zeldovich (see [6], in the book by Frank-Kamenetsky), it may be considered that the rate of the process as a whole is determined either by the rate of transfer of the substance in the outer volume (if diffusion in the outer volume, or "external" diffusion, is small), or by the rate of transfer

of the substance within the solid (if the rate of reaction, or the rate of transfer of the substance within the solid, or the rate of "internal" diffusion, is low). Thus, the rate of reaction as a whole is determined either by the reaction in the "external diffusion region" or by that in the "internal kinetic region." The latter only occurs when the rate of chemical reaction is very low, and is hardly possible in the present case. On the conditional assumption that hydrate cellulose film is microporous, and that the reaction of the OH groups of cellulose with OH ions obeys a first order equation, it is possible to calculate approximately in which cases the reaction is determined by the "external diffusion region" and is accelerated by stirring, and in which cases the reaction is determined by the "internal diffusion region" and its rate is not affected by stirring. The reaction proceeds in the "external diffusion region" if

$$\frac{Nu}{d} D_1 < \sqrt{D_T k}, \quad (5)$$

where Nu is Nusselt's dimensionless parameter; k is the chemical reaction rate constant; D_1 is the coefficient of diffusion in the external liquid ("coefficient of external diffusion"); D_T is the coefficient of diffusion within the film ("coefficient of internal diffusion"); d is a measure of the film thickness.

In this case the value of k is not known, as the rate of reaction of OH groups in water or OH ions in caustic soda with OH groups in cellulose was not measured. Assuming conditionally that this value, by analogy with the rate constant for the hydrolysis of cellulose in an acid medium, is 10^{-4} , and knowing that for films usually,

$\frac{Nu}{d} \approx 1$, and the value of D_1 for external diffusion is usually $\sim 10^{-5}$, we can calculate approximately the values of $\frac{Nu}{d} D_1$ and $\sqrt{D_T k}$. In the present case they are, respectively, for the diffusion of caustic soda:

$$\frac{Nu}{d} D_1 \approx 10^{-5}; \quad \sqrt{D_T k} \approx 10^{-5},$$

and for the diffusion of methylene blue:

$$\sqrt{D_T k} \approx 3 \cdot 10^{-6}$$

As these preliminary calculations show, in both cases the values of $\frac{Nu}{d} D_1$ and $\sqrt{D_T k}$ are of the same order, and stirrings should affect the diffusion process as a whole. In fact, the diffusion coefficient D , calculated from Equation (2), for the diffusion of NaOH with vigorous stirring of the solution (1200 rev/min) is 1.375 times as great as the coefficient without stirring. In the same conditions, the diffusion of methylene blue is only 1.20-1.24 times as rapid with stirring. When the coefficient of internal diffusion decreases to 10^{-8} , the value of $\sqrt{D_T k}$ becomes equal to 10^{-6} ; that is, less than the value of $\frac{Nu}{d} D_1$, and stirring should no longer affect the diffusion rate as a whole. Indeed, in the nonsteady course of the process at the start of diffusion or during sorption of various substances by hydrate cellulose film ($D' \approx 10^{-9} \text{ cm}^2/\text{sec}$), stirring of the liquid has no influence on the rate of diffusion or sorption.

These experimental results show that the diffusion rate depends on the degree of swelling of the hydrate cellulose film in the given medium, and on the molecular weight of the diffusing substance. Undried films and those which had not been mechanically stretched have a more loose molecular structure than films dried under tension at elevated temperatures. Therefore water and OH ions penetrate more easily into the structure of undried hydrate cellulose films; this, in turn, produces greater swelling and leads to an increase of the coefficient D proportionally to the percentage swelling.

When hydrate cellulose swells in water or in solutions, OH groups of water or OH ions become joined to OH groups of the cellulose molecules, with a corresponding weakening of the hydrogen bonds between the OH groups of adjacent cellulose molecules. The weakening of these hydrogen bonds, in its turn, leads to a certain displacement of the macromolecules, and to an increase in the diameter of the internal intermolecular pores. Increase of pore diameter in a solid leads to an acceleration of diffusion within the solid, and to an increase of the value of D . Experimental data show that in the swelling of hydrate cellulose films in water or in aqueous solutions, the increase of the diffusion coefficient D is approximately directly proportional to the percentage swelling of hydrate cellulose in water. On the other hand, the diffusion coefficient D varies in inverse proportion to the molecular weight of the diffusing substance (see the equation in [4]). Therefore at constant temperature the value of the diffusion coefficient varies according to the empirical relationship -

$$D = k_1 D_0 \sqrt{\frac{M_2}{M_1}} \quad (6)$$

The diffusion of OH ions is more rapid than the calculated value. This increase, in comparison with the calculated value, is particularly marked in more concentrated solutions of NaOH, and may be explained by the electrical charge on the OH ions.

The rate of diffusion in the initial nonsteady period is considerably less than the rate of diffusion in steady conditions. This is understandable if one considers the great influence weakening of the hydrogen bonds has on the rate of diffusion as the result of swelling of hydrate cellulose film in water or by the action of OH ions. In the initial period, diffusion occurs in conditions of the initial strength of the hydrogen bonds between the OH groups of hydrate cellulose, that is, in conditions closely resembling the diffusion of hydrogen and other substances which do not react with OH groups of cellulose. Therefore, in nonsteady conditions, the value of $\underline{D'}$ is $\sim 10^{-9}$ – 10^{-10} , which is in good agreement with Reitlinger's data for hydrogen [1] and with our data for nonsteady diffusion of cuprammonium solution into hydrate cellulose fibers.

The data of Table 2 show that the value of the diffusion coefficient $\underline{D'}$ for nonsteady conditions depends on preliminary drying of the film, and on the nature of the diffusing substance. Drying of the film strengthens the intermolecular structure (hydrogen bonds) and retards the penetration of water molecules. The penetration of OH ions is more rapid than the penetration of water molecules, and the value of $\underline{D'}$ is several times greater.

In steady conditions, the concentration of OH ions in NaOH solution has little effect on the value of \underline{D} . The explanation is that in our chosen conditions, the OH ion concentration is so great in all cases (pH varies between 13.5 and 14.0) that a small change of concentration has no appreciable effect on the weakening of the intermolecular bonds. The complete absence of any effect of the concentration of substances such as glycerin or methylene blue is explained by the fact that weakening of intermolecular bonds is produced by molecules of water and not of the dissolved substance.

The arbitrary values of the activation energy of the diffusion process $\underline{E_D}$ for various cases of steady state diffusion also vary within insignificant limits, and are considerably less than the corresponding values obtained for the nonsteady diffusion process [5]. The explanation is that as the intermolecular hydrogen bonds between the macromolecules become weakened, the effect of temperature is less than at lower temperatures. For the same reason, the values of $\underline{E_D}$ are somewhat less for the diffusion of NaOH than for the diffusion of methylene blue or glycerin, as in the latter case, there is more intermolecular bonding between the cellulose molecules.

SUMMARY

1. The diffusion of various substances through hydrate cellulose films is determined by the degree of swelling of the film in the diffusing medium, and by the molecular weight of the diffusing substance. The relationship is given by Equation (6).
2. The different rates of diffusion in dried and undried films are explained by the different degrees of swelling in the diffusion medium. Diffusion is more rapid through the more loose undried films, as into the more "loose" unstretched or strongly swollen fibers.
3. Diffusion is much slower in nonsteady than in steady conditions, as at the beginning of the process the diffusing substance meets the strong original structure of the film in the form of stable hydrogen bonds between the cellulose molecules.
4. The value of the diffusion coefficient for nonsteady conditions is in good agreement with data for steady diffusion of substances which do not cause swelling of hydrate cellulose, and also agrees with data obtained for nonsteady sorption of copper by hydrate cellulose fibers.
5. Stirring affects the rate of diffusion only in the range of diffusion coefficients from 10^{-5} to 10^{-7} ; that is, in conditions of diffusion through or into liquid or strongly swollen substances. Stirring has no effect on the rate of diffusion of substances which do not cause swelling, or on the rate of diffusion in nonsteady conditions.

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ION EXCHANGE HETEROGENEOUS REACTIONS

II. DEPENDENCE OF ION EXCHANGE ON RESINS

ON THE DILUTION OF SOLUTIONS

K. M. Saldadze and E. A. Bozhevolnov

The question of the dependence of ion absorption by resins on dilution is of theoretical importance in studying the quantitative laws which apply to ion exchange processes. Up to the present time this question has been studied on soils, aluminosilicates, permutites, etc [1-4]. In particular, Gapon [5], on the basis of the equation for the exchange sorption isotherm, showed that the quantity of cations absorbed by soil is independent of dilution if the absorbed cations are of the same valency, and dilution increases sorption of ions of higher valency if the exchanged ions have different valencies.

The question of the dependence of exchange sorption on dilution has again become very important in studies of ion exchange on the new ion-exchange materials, with the use of synthetic resins in various branches of industry.

The following systems were investigated in order to study this question:

- | | | | |
|--------------------|-------------------|----------------|---------------|
| 1. $RMg + Ba^{2+}$ | 3. $RH + Ba^{2+}$ | 5. $RBa + K^+$ | 7. $RH + K^+$ |
| 2. $RK + Ba^{2+}$ | 4. $RBa + H^+$ | 6. $RK + H^+$ | |

In the first, sixth, and seventh cases, on the basis of the laws established by Gapon [5], one should expect that the quantity of absorbed ions should not change with dilution; in the second and third cases, the amount of absorbed barium should increase with dilution; and in the fourth and fifth cases, the amounts of absorbed hydrogen or potassium should decrease with dilution.

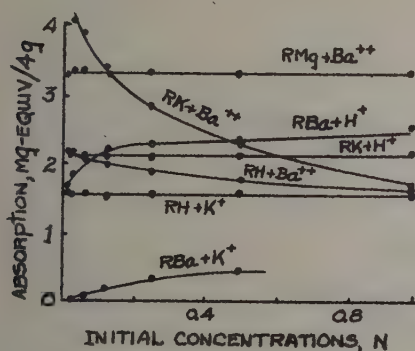


Fig. 1. Absorption of various cations on Wofatit R resin.

the exchange of univalent ions for bivalent ions on the resin. When cations of equal valency are exchanged, the absorption of cation does not vary with dilution. This behavior is seen in all the resins studied, which contain either sulfo groups (SBS resins) or sulfo groups and phenolic groups (resin R), or carboxyl and phenolic groups (resin S). Thus, general laws of ion exchange are seen here, which apply both to soils and to different synthetic resins.

The following cation-exchange resins were used in the investigation: SBS resin, Wofatit R and Wofatit S, previously saturated with hydrogen, potassium, magnesium, or barium ions. The amounts of resin taken were in each case 2 g (SBS resin) and 4 g (R and S resins). The initial quantity of the cation used for the exchange was 5 mg equivalent in each case, and the solution volumes were varied so as to obtain the following series of initial concentrations: 1, 0.5, 0.25, 0.125, 0.0625, 0.025 and 0.01 N.

After the resins had been in contact with the solutions for four days, the equilibrium solutions were analyzed polarographically, which made it possible to calculate the amounts of absorbed ions. The results of these experiments are shown in Figs. 1-3. It is seen from these figures that when a bivalent ion is exchanged for a univalent ion on the resin, the absorption of the bivalent ion increases with dilution of the solution. The reverse is seen in

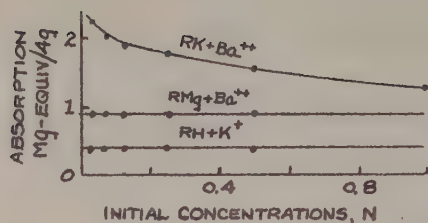


Fig. 2. Absorption of various cations on Wofatit S resin.

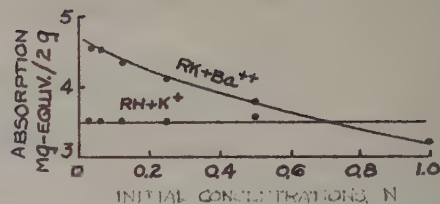


Fig. 3. Absorption of various cations on SBS resin.

To explain the effects described, let us represent the ion exchange process as a chemical reaction which follows the equation:



To express the isotherm of the ion exchange reaction, we adopt Nikolsky's equation [6] without taking activity coefficients into account:

$$\frac{g_1^{1/z_1}}{g_2^{1/z_2}} = K \frac{c_1^{1/z_1}}{c_2^{1/z_2}} \quad (1)$$

The following notation is used: \underline{S} is the absorption capacity of the cationic resin in mM/g; \underline{a}_2 is the quantity of \underline{M}_2 ions absorbed in the exchange reaction in mM/g; \underline{m}_2 is the initial quantity of ions of \underline{M}_2 in the solution taken, in mM; \underline{V} is the volume of the solution in liters; \underline{p} is the weight of resin in grams; \underline{z}_2 is the valency of the sorbed cation; \underline{z}_1 is the valency of the desorbed cation. The equilibrium concentration of the desorbed cation \underline{M}_1 will then be:

$$c_1 = \frac{z_2 a_2 p}{z_1 V} \quad (2)$$

and the equilibrium concentration of the sorbed ion \underline{M}_2 :

$$c_2 = \frac{m_2 - a_2 p}{V} \quad (3)$$

At equilibrium the amounts of the sorbed ion \underline{M}_2 and of the ion \underline{M}_1 in the resin will be:

$$g_2 = p a_2; \quad g_1 = \frac{p S z_1 - p a_2 z_2}{z_1}$$

and Equation (1) is then written in the following form:

$$\frac{\left(\frac{p S z_1 - p a_2 z_2}{z_1} \right)^{1/z_1}}{(p a_2)^{1/z_2}} = K \frac{\left(\frac{a_2 p z_2}{z_1} \right)^{1/z_1}}{(m_2 - a_2 p)^{1/z_2}} V^{1/z_2 - 1/z_1} \quad (4)$$

Hence it follows that in the exchange of ions of equal valency, when $\underline{z}_2 = \underline{z}_1$ (cases one, six, and seven), the following equation corresponds to the equilibrium state:

$$\frac{p S - p a_2}{p a_2} = K \frac{a_2 p}{m_2 - a_2 p} \quad (5)$$

that is, for a constant value of the initial amount of the \underline{M}_2 ion, the amount sorbed will be constant, irrespective of dilution (when $\underline{z}_2 = \underline{z}_1$, the term $V^{1/z_2 - 1/z_1} = 1$).

If we now suppose that $\underline{z}_2 > \underline{z}_1$ (case two and three), then the fraction in the first part of equation (4) decreases with dilution, and therefore, the amount of the second cation sorbed decreases. When $\underline{z}_2 < \underline{z}_1$, the reverse is found, for the same reason.

From these results it may be concluded that ion exchange reactions on resins obey the Mass Action Law.

SUMMARY

1. In ion-exchange sorption of cations on synthetic resins, the quantity of sorbed cations is independent of dilution if the exchanged cations have the same valency, and dilution increases the sorption of the ion with greater valency if the exchanged ions have different valencies; thus, the laws established by Gapon [5] and Nikolsky [6] for soils and permutites are confirmed.

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THE HARDENING OF PHENOL-FORMALDEHYDE RESINS

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Phenol-formaldehyde resins are divided into two groups according to the ratio of the original components and the catalyst used for the condensation: thermoreactive resole resins, which pass into resitols and resites on heating (completely insoluble and infusible), and thermoplastic novolak resins, capable of passing into the infusible and insoluble state after supplementary treatment with formaldehyde or hexamethylene tetramine [1].

In the present investigation a study was made of the hardening process of novolak phenol-formaldehyde resin on addition of hexamethylene tetramine (urotropine) at different temperatures.

We used the method proposed by Slonimsky, Kargin, and Golubenkova [2], and used by them in investigations of the hardening process of phenol-formaldehyde resoles, the hardening stages of the novolak resin being characterized by the intrinsic viscosity of solutions of the resin in ethyl alcohol and cyclohexanone. The resin gels (hardened with small additions of urotropine) with different contents of solvent were studied by means of thermo-mechanical curves obtained with the aid of V. A. Kargin's dynamometric balance. The nonswelling, hardened resins were evaluated by their deformation behavior under different stresses with the aid of S. N. Zhurkov's apparatus.

The results obtained in studies of the solubility of novolak resin with different additions of urotropine (hardened at different temperatures) in cyclohexanone at 100° make it possible to distinguish three physical stages during hardening of the resin (Fig. 1).

Soluble resins. Resins with a urotropine content below 1%, obtained at any hardening temperature, and also with any urotropine content, but at hardening temperatures up to 120°, are completely soluble. Fig 2 shows the dependence of the reduced viscosity on concentration of solutions of novolak resin in cyclohexanone and ethyl alcohol. As the urotropine content changes from 0.1 to 0.5%, there is no appreciable variation of the dependence of η_{sp}/c on c ; as the graph shows, the relationships obtained lie on the same straight line. The intrinsic viscosity of novolak resin solutions ($\lim_{c \rightarrow 0} \frac{\eta_{sp}}{c}$) is 7.75 in ethyl alcohol and 8.75 in cyclohexanone.

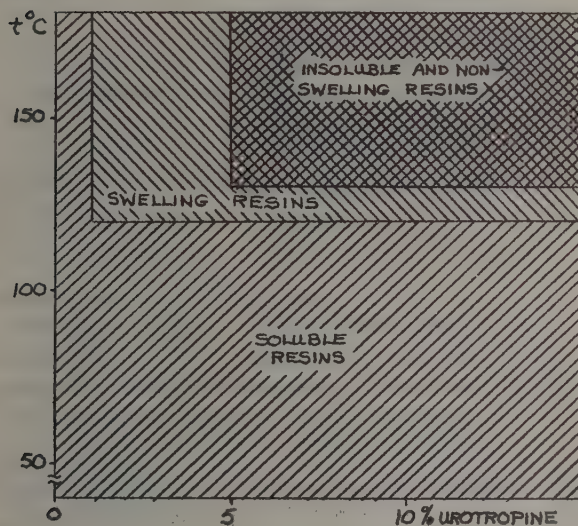


Fig. 1. Schematic representation of the hardening of phenol-formaldehyde novolak resins.

In this stage novolak resins do not have a network structure and are characterized by high plastic deformations and high brittleness.

Swelling resins. With urotropine contents from 1 to 5% and at hardening temperatures above 120°, and also with urotropine contents over 5% and at hardening temperatures of 120-130°, novolak resins are characterized by swelling and partial solubility in solvents, and the gels obey Hooke's law. Increase of the urotropine content from 1 to 5% decreases the residual deformation.

Fig. 3 shows thermo-mechanical curves for gels hardened at 120° with 30% cyclohexanone solvent and different additions of urotropine. With a urotropine content of 1%, from 70° upward, irreversible flow takes

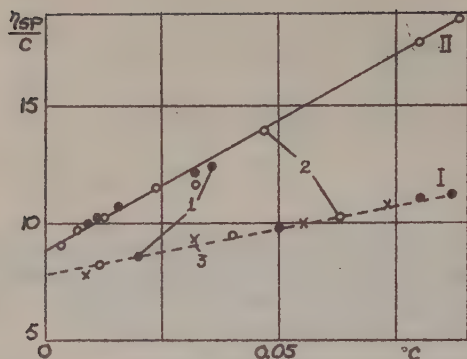


Fig. 2. Reduced viscosity of novolak resin solutions: I - in ethyl alcohol; II - in cyclohexanone; 1 - the original resin; 2 - with a content of 0.1% urotropine, and 3 - 0.5% urotropine.

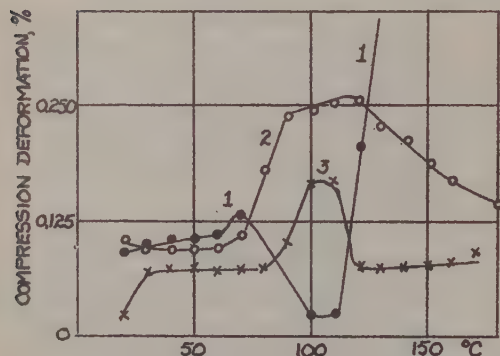


Fig. 4. Compression deformation of gels containing 30% cyclohexanone, hardened at 180° with urotropine contents: 1 - 1%; 2 - 3%; 3 - 5%.

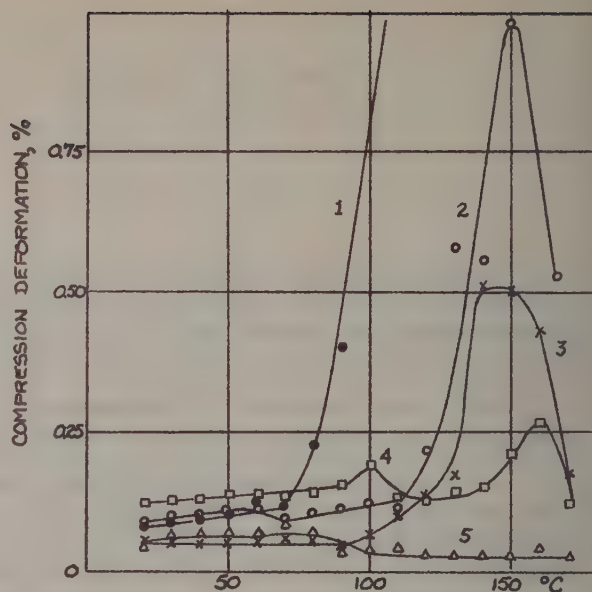


Fig. 3. Compression deformation of gels containing 30% cyclohexanone, hardened at 120° with urotropine contents: 1 - 1%; 2 - 3%; 3 - 10%; 4 - 13%; 5 - 15%.

place. As the urotropine content increases (above 1%) the value of the maximum deformation decreases and the softening temperature increases. At 150-180° there is a sharp decrease of deformation as the result of vigorous development of the hardening process.

Fig. 4 shows thermo-mechanical curves for gels with 30% content of solvent, hardened at 180°.

As Fig. 4 shows, at higher temperatures the hardening process is more complete. Apparently at this stage of hardening, a thin network structure, characterized by mobility, is formed in the resin, as is indicated by the existence of considerable residual deformation.

Fig. 5 shows the process of bond rupture in the gel on addition of larger amounts of cyclohexanone solvent. This is seen in novolak resin gels containing 1 and 3% urotropine. However, it was not possible to bring about bond rupture in a gel with 5% urotropine (Fig. 5) even on the addition of the maximum amount of solvent. Fig. 7 clearly shows the reversibility of the bonds in the gel. The curve for the gel with a solvent content of 87% shows flow, indicating bond rupture taking place in the gel. The reversibility of the bonds in the gel (restoration of ruptured bonds or formation of new ones) is confirmed by the complete co-incidence of the curves for the original specimen and the specimen dried after swelling.

The energy of formation of cross-links in the structural network of the resin was calculated from the dependence of the equilibrium modulus of elasticity on temperature, for a gel of a resin with 1% urotropine and 30% cyclohexanone. The value found, $\bar{U} = 5.7$ kcal/mole bonds, agrees with the energy of the hydrogen bond and coincides with the value [2] for resites (hardened resole resins). The results show that hydrogen bonds play a significant role in the hardening processes of resins.

Nonswelling and insoluble resins. At urotropine contents above 5% and hardening temperatures above 130°, novolak resin yields almost insoluble, nonswelling and nonsoftening products, which may be the sign of formation of a denser network structure.

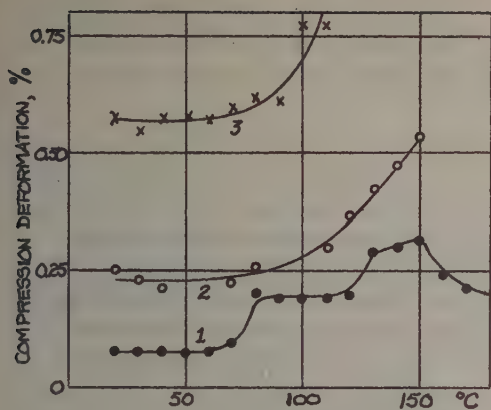


Fig. 5. Compression deformation of gels hardened with 1% urotropine at 150°, containing: 1 - 29%; 2 - 52%; 3 - 67% cyclohexanone.

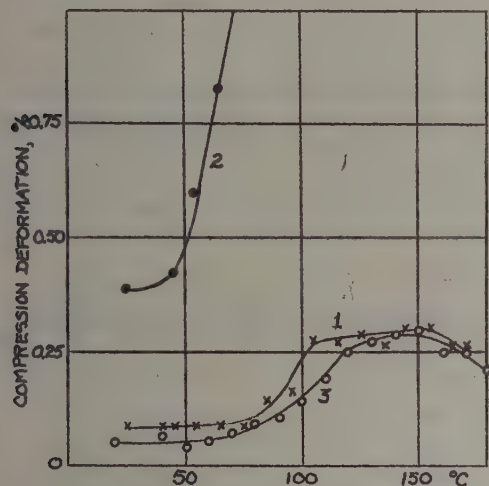


Fig. 7. Compression deformation of gels hardened with 1% urotropine at 150°; 1 - in the original state; 2 - with a content of 87% cyclohexanone; 3 - the same, after drying at 150°.

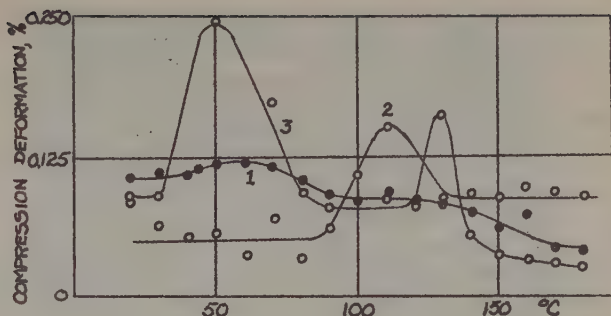


Fig. 6. Compression deformation of gels hardened with 5% urotropine at 150°, containing: 1 - 13%; 2 - 25%; 3 - 30% cyclohexanone.

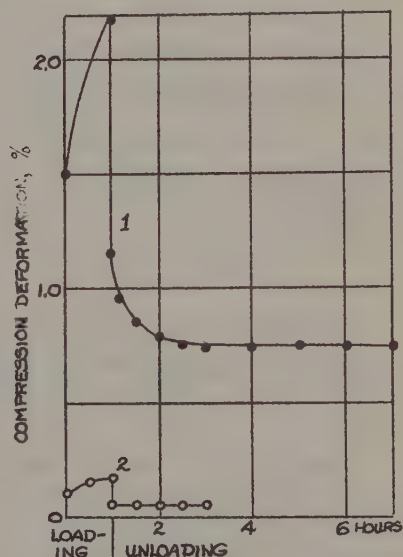


Fig. 8. Variation of the elasticity of the hardened resin on repeated application of stress (20 kg/cm² at 160°); 1 - first loading; 2 - repeated loading.

Analogously to the changes of the equilibrium modulus under repeated load, the resins also undergo changes in the value of the residual deformation. However, this value remains considerable, and may be attributed both to the presence of a resin fraction of a low degree of hardening (the solubility of novolak resin hardened at 180° with addition of 15% urotropine is 27%), and to further hardening which takes place under the influence of the applied force. This hardening process leads to the formation of new bonds and prevails over the concurrent process of the disruption of existing bonds. Development of the hardening process under the action of the force causes fixation of the high-elastic deformation, which prevents the restoration of the original form of the specimen.

Fig. 8 shows the change in the elasticity of a hardened resin under the repeated action of the same stress (20 kg/cm² at 160°).

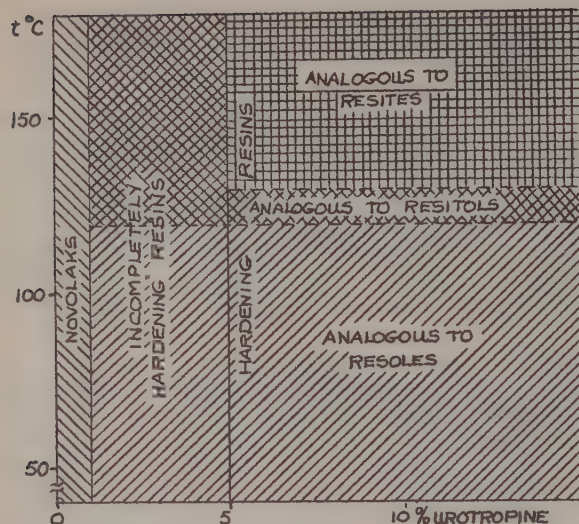


Fig. 9. Hardening conditions of novolak resins, schematic.

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The resin becomes increasingly stronger under the action of the applied force. The value of the modulus under the first stress is 920 kg/cm^2 , and this becomes $12,000 \text{ kg/cm}^2$ on repeated loading.

SUMMARY

Three regions of urotropine content in novolak resins may be recognized according to the hardening ability (Fig. 9):

- 1) with a urotropine content below 1%, the resins retain the nature of novolaks and do not harden;
- 2) with urotropine contents from 1 to 5%, the resins are capable of partial hardening, forming, in two stages, swelling and incompletely soluble products;
- 3) with a urotropine content above 5%, the resins become completely hardenable, and show three stages of hardening, analogously to the resole resins (resole, resitol, resite).

CERTAIN LAWS OF THE BUTTER CHURNING PROCESS

V. N. Shuvalov and I. N. Vlodavets

The process of churning butter from cream has been studied very little from the quantitative aspect, which is apparently to be explained by the considerable complexity of the process, and the multiplicity of factors which must be taken into account for its comprehensive evaluation. At the same time, problems in improving the production of butter insistently demand the elucidation of the fundamental quantitative laws which govern the conversion of cream into butter.

In the present state of the problem, it is difficult to speak of any universal theory of butter formation. The creation of such a theory is a matter for the future; it should unify and explain the physico-chemical and hydrodynamic laws which may be derived from sufficiently strictly controlled experiments. The present communication is deliberately restricted to an attempt at establishing certain particular laws which follow from our observations.

The experimental equipment in which cream was converted into butter was described previously by one of the present authors [1]. It consisted of a cylinder of organic glass containing a rotating stirrer (with blades or cylindrical). The cylinder contained pasteurized cream, which had been subjected to preliminary physical aging for 12-14 hours at 5-6°. The fat content of the cream was determined by the standard sulfuric acid method. The initial churning temperature was kept strictly constant (10°) and was controlled with the aid of a copper-constantan thermocouple, connected to a sensitive mirror galvanometer. The rotation speed of the stirrer was controlled with a precision tachometer, and was kept constant with an accuracy of ± 0.2 rev/sec. The churning time τ , which was the time elapsed from the start-up of the stirrer to the instant of appearance of clearly distinguishable grains of butter, was measured by means of a seconds clock. The power required for beating the cream with the stirrer was measured with a torsional dynamometer.

By using interchangeable stirrers, it was possible to vary the geometrical conditions of churning. The rotation speed was varied in the limits of 8 to 24.6 rev/sec. The fat content of the cream was varied in the limits of 20 to 50%. When blade stirrers were used, the degree of filling the cylinder with cream was also varied. With smooth cylindrical stirrers, churning took place with different sized gaps between the inner and outer cylinders.

From the results of observations made at different degrees of filling of the vessel, it may be concluded that the presence of a relatively large cream/air area of separation considerably accelerates the process of butter formation. This is particularly true for cream with a low fat content. With cream of high fat content, the effect of free surface is considerably less. Consequently, from the specific consumption of mechanical energy in the treatment of one kilogram of cream of low fat content, blade stirrers are more efficient, as they ensure better inclusion of air into the cream so that the maximum free surface is formed, while for beating cream of high fat content smooth cylindrical stirrers are sufficiently effective.

These results indicate that the presence of cream/air boundary surfaces and the associated flotation effects, studied in detail by Belousov [2], is a factor which, although very favorable to the butter-making process, is not obligatory for its success.

On the assumption that the formation of butter from cream by mechanical stirring can be regarded as a process of coagulation of colloidal particles, one of the present authors [3] derived the following kinetic equation for the ideal case of laminary flow:

$$-\frac{dv}{d\tau} = k_1 \varphi \frac{v}{a}, \quad (1)$$

where v is the number of particles of fat in unit volume of cream; τ is the time; φ is the content of fat in unit volume; v is the rate of displacement of the outer layer of cream; a is the thickness of the layer. The constant k_1 includes a particle collision effectiveness factor and is a function of the composition of the whey, of the temperature, and other physico-chemical characteristics of the cream.

The duration of churning of the cream, τ , which may be defined as the time required for the average size of the fat particles to increase from a certain quite definite initial value, corresponding to the average number of

fat particles in unit volume, ν_0 , to a certain other value, which corresponds to the average number of fat particles in unit volume, ν_k , may be expressed by the following formula, obtained by integration of equation (1):

$$\tau = \frac{a (\ln \nu_0 - \ln \nu_k)}{k_1 \varphi v} = \frac{k}{\varphi v} \quad (2)$$

Thus, if we neglect the effect of the gaseous phase and flotation processes, the duration of churning of cream in laminary flow should be inversely proportional to the fat content of the cream and the rate of displacement of the outer layer.

Studies of the hydrodynamic conditions of cream churning in our experimental apparatus showed that both with blade and with cylindrical stirrers, churning takes place in the turbulence region. In conditions of turbulence, equation (2), naturally, ceases to be valid. Nevertheless, as Grishchenko's experiments [4] showed, even in the turbulence region, the number of particles of fat in unit volume decreases during churning according to the equation:

$$-\frac{d\nu}{d\tau} = k_2 \nu, \quad (3)$$

which differs from equation (1) only by the indeterminate nature of the constant.

Attempts to calculate the coagulation rate constant for turbulent flow, known from the literature [5-7] by no means exhaust the question. It may be assumed that this constant should be expressed as a function of certain dimensionless quantities. However, this should result in a certain correlation between the expressions valid for the turbulence region, and equations (1) and (2), derived for the laminary region.

In the absence of adequate data for establishing the precise form of the rate constant k , we may meanwhile note certain interesting features of the dependence of the duration of churning, τ , on the fat content φ of the cream and on the rate of displacement of the outer layer of cream v , which is taken as the peripheral speed of the stirrer in cm/sec.

Fig. 1 shows in graphical form the results of three series of experiments in which the dependence of churning time on the fat content of the cream was studied. The slope of the line 1 leads to the relationship:

$$\log \tau = \log k - 3.12 \log \varphi \quad (4)$$

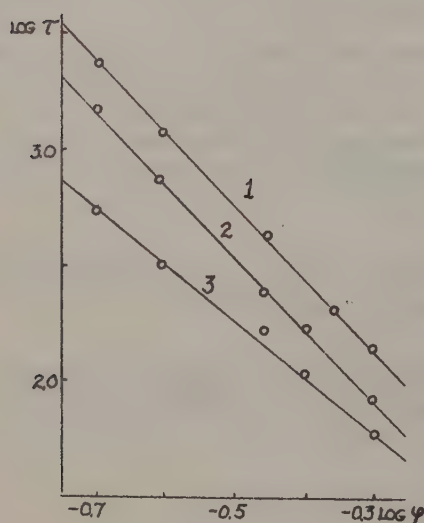


Fig. 1. Dependence of $\log \tau$ on $\log \varphi$ during churning of butter in a vessel of 13.0 cm diameter by stirrers rotating at 16 rev/sec: 1 - smooth cylindrical stirrer 10.5 cm diameter; 2 - ditto, 12.5 cm diameter; 3 - two-blade stirrer.

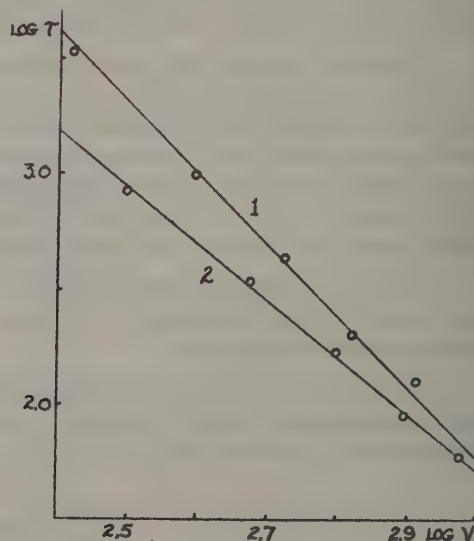


Fig. 2. Dependence of $\log \tau$ on $\log v$ during churning of butter in a vessel of 13.0 cm diameter by stirrers: 1 - smooth cylindrical stirrer, 10.5 cm diameter; 2 - two-blade stirrer. Fat content of the cream, 35% ($\varphi = 0.35$).

or

$$\tau = \frac{k}{\varphi^{3.12}} \quad (5)$$

where $k = 16.2$. In the case of line 2, a completely analogous relationship holds:

$$\tau = \frac{k}{\varphi^{3.15}} \quad (6)$$

where the value of the constant $k = 10.3$. The difference between the values of the constants is apparently due to differences in geometrical conditions of churning, but this difference does not affect the general nature of the dependence of duration of churning on the fat content in the cream. The difference of the exponent of φ is quite insignificant and may be explained by experimental errors and the approximate nature of the curve construction.

A two-blade stirrer produces flow with different hydrodynamical characteristics; the dependence of duration of churning on the fat content (Curve 3, Fig. 1) is somewhat different:

$$\tau = \frac{k}{\varphi^{2.44}} \quad (7)$$

In this case the constant k is equal to 11.1.

The effect of the rotation speed of the stirrers on the duration of churning is shown in Fig. 2. In the churning of cream containing 35% fat, that is, when $\varphi = 0.35$, the dependence of the duration of churning on the speed of a cylindrical stirrer (Curve 1) may be expressed by the formula:

$$\tau = \frac{k}{v^{3.10}} \quad (8)$$

where $k = 11.5 \cdot 10^{10}$. It is interesting that the exponent of v in formula (8) is practically the same as the exponent of φ in formula (5), which applies to the same geometrical conditions of churning.

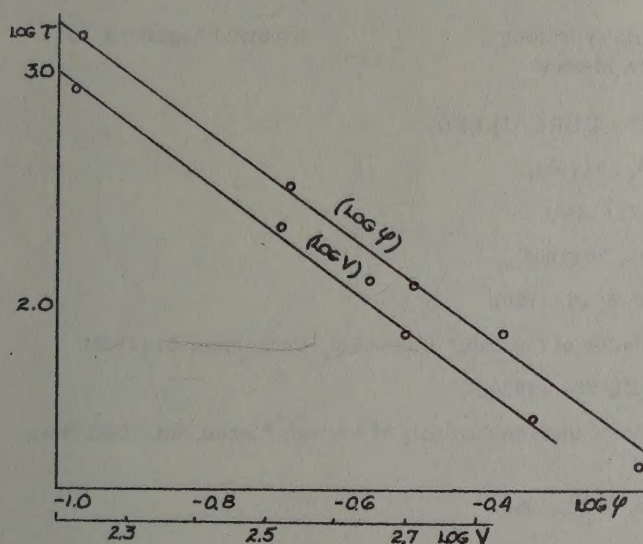


Fig. 3. Dependence of $\log \tau$ on $\log \varphi$ and $\log v$ in churning of butter (Recalculation of Grishchenko's results).

$$\tau = \frac{k}{(\varphi v)^n} \quad (10)$$

where k is a constant, and the exponent of n for smooth cylindrical stirrers is 3.1 and for two-blade stirrers, 2.5. The values of the exponent of n are apparently subject to considerable variations according to the geometrical conditions of churning.

We have examined the data of Grishchenko [8], who attempted to reconcile the results of his experiments with the so-called hydrodynamical theory of butter formation, in which decisive significance is attached to the separating action of eddies which arise in turbulent flow. The formulas which he proposes are only in very approx-

The effect of the rotation speed of a two-blade stirrer on the duration of churning, corresponding to the Curve 3 in Fig. 1, is shown in the form of Curve 2 in Fig. 2. This relationship may be expressed by the formula -

$$\tau = \frac{k}{v^{2.46}} \quad (9)$$

where $k = 0.124 \cdot 10^{10}$. It is again found that the exponent of v in formula (9) is almost exactly equal to the exponent of φ in formula (7), which applies to the same geometrical conditions of churning.

Thus, the dependence of the duration of churning on the content of fat in the cream and on the rotation speed of the stirrer may be expressed by the following formula, valid for the speed and concentration limits indicated above, on the basis of the above results:

imate agreement with his experimental data, despite their considerable complexity. The results of our calculations, based on Grishchenko's data, are shown in Fig. 3, which gives the dependence of $\log \tau$ on $\log \varphi$ and $\log \underline{v}$, respectively. In the analytic form these relationships are expressed by the formulas:

$$\tau = \frac{k}{\varphi^{2.15}} \quad \text{and} \quad \tau = \frac{k}{\varphi^{2.18}} \quad (11)$$

The difference between the exponents \underline{n} in the two formulas is so small that it may be confidently asserted that our formula (10) is also applicable in this case, and the exponent \underline{n} may be taken as 2.2.

Comparison of the empirical formula (10) with the formula (2), derived on the assumption that the butter churning process may be considered as a process of coagulation of fat particles, in the case of laminary flow, readily shows that equation (2) is a special case of equation (10), when $\underline{n} = 1$. We may suppose that the product $\varphi \underline{v}$ is a component of some dimensionless criterion, of which the coagulation rate constant in equation (3) for turbulent flow is a function. As, however, this product has definite dimensions, the supposed criterion must also include other factors, the determination of which must be the aim of further experimental investigations.

SUMMARY

It is shown that the dependence of the duration of churning of butter from cream, τ , on the fat content, φ , and the rotation speed of the stirrer, \underline{v} , is satisfactorily described by the empirical formula:

$$\tau = \frac{k}{(\varphi \underline{v})^{\underline{n}}},$$

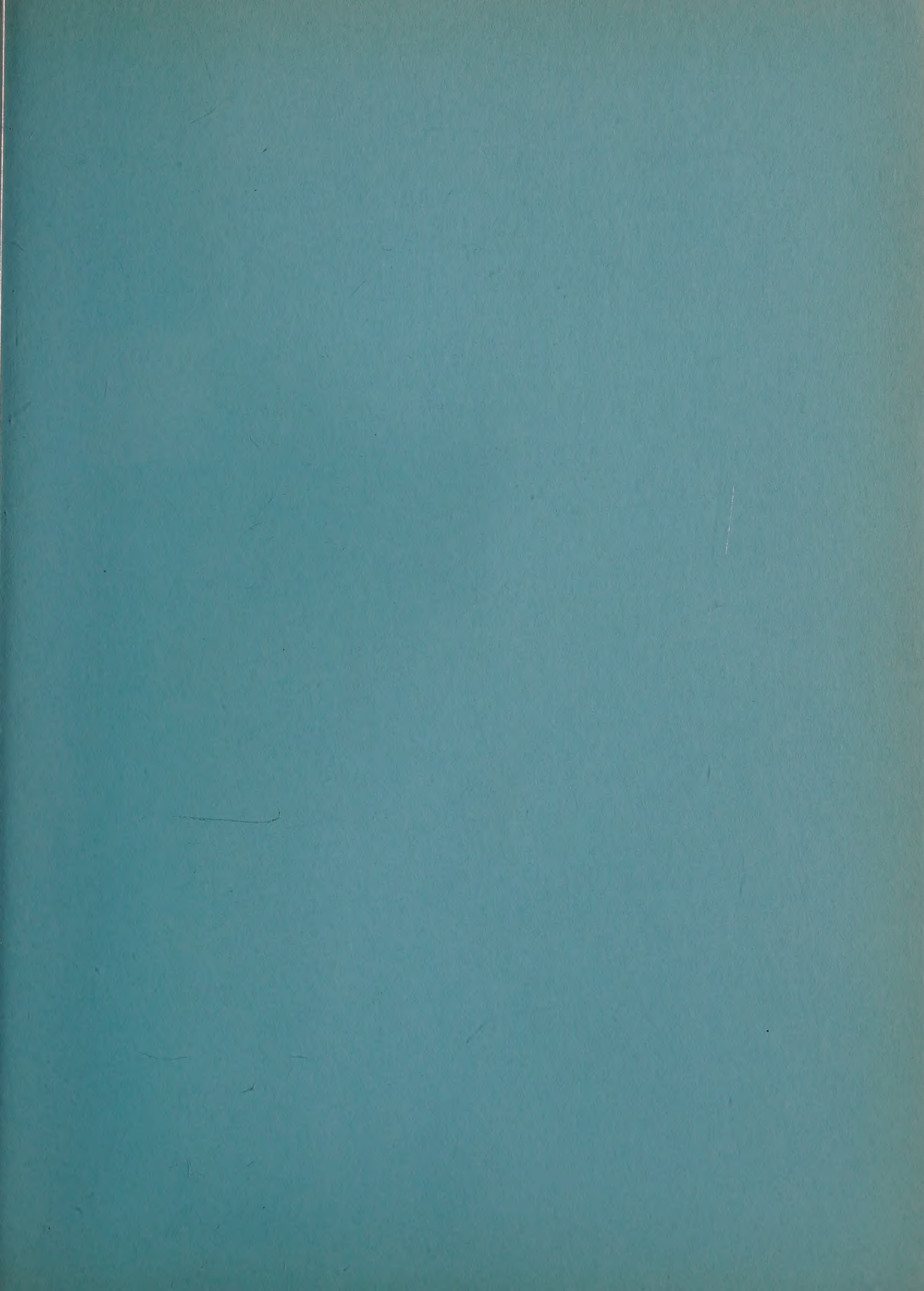
where the exponent \underline{n} depends on the hydrodynamic conditions of churning. When $\underline{n} = 1$, this formula agrees with the formula derived from the concept of butter formation as a process of coagulation of colloidal fat particles in laminary flow.

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